

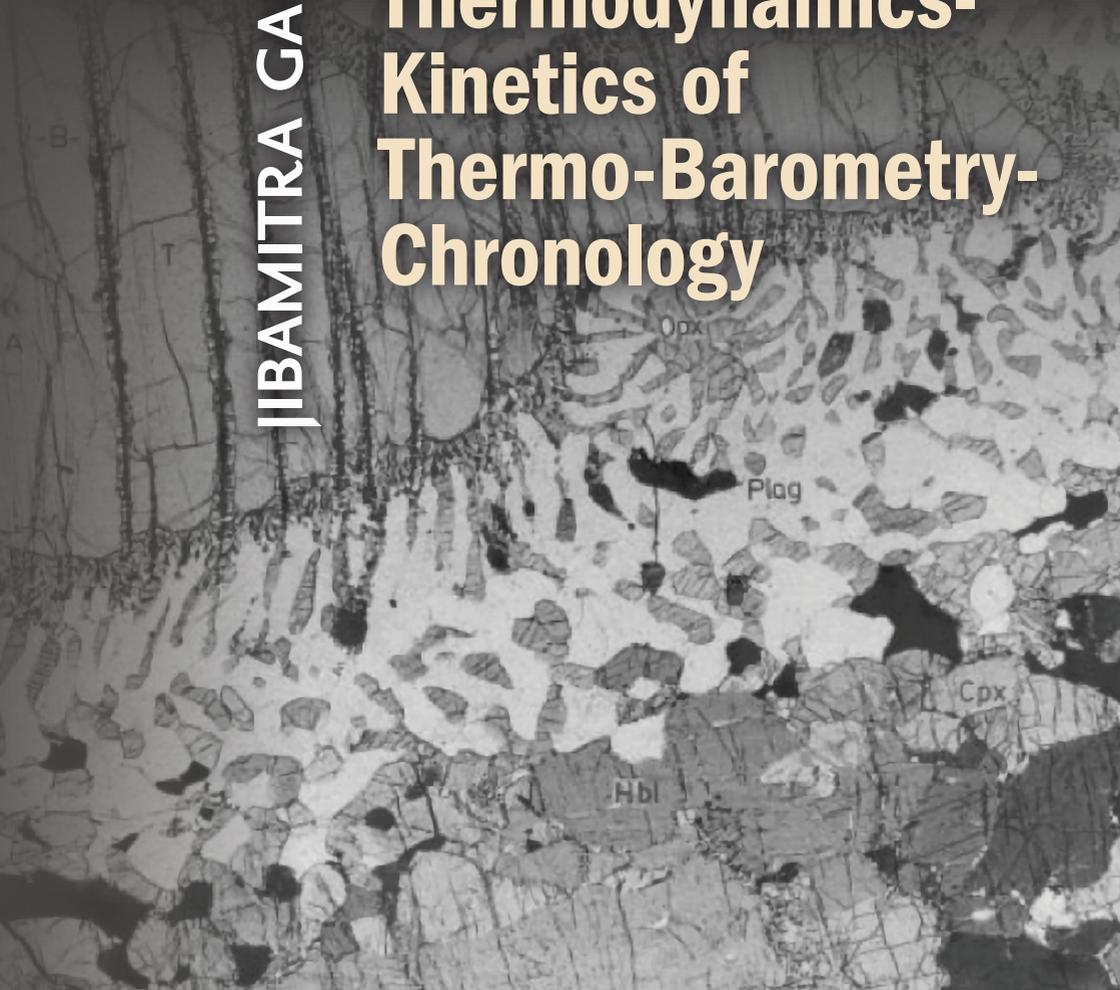
Geochemical Perspectives



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JIBAMITRA GANGULY

Academic Reminiscences and Thermodynamics- Kinetics of Thermo-Barometry- Chronology





Each issue of *Geochemical Perspectives* presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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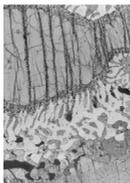
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About the cover

Photomicrograph of a garnet crystal showing two sets of fracture-reaction textures that resulted from metamorphisms at ~1000 Ma and ~500 Ma. The thermal history of the latter, which was related to the Pan-African collision event, has been constrained by reaction-diffusion modeling of compositional zoning in the garnet. MODIFIED FROM GANGULY ET AL. (2001)

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PREFACE

In my web page, I divided my research contributions into eight topical groups. However, in all but one, thermodynamics or diffusion kinetics or both constitute important components of my research and publications. The present contribution is focused on two specific topics related to these two fundamental disciplines. These are preceded by some of my academic reminiscences that have also been sprinkled in different sections when they relate to some interesting or important history behind specific research contributions.

I have tried to write each section to show the important steps in its historical development, as they stand out in my analysis and understanding of the subjects, and to keep the presentation as non-technical as possible so it may be read by a wide audience with a modest background of thermodynamics and diffusion kinetics. I did not attempt to write a thorough review of the subject matter reflected in the title. Instead, this article is an account of a segment of my personal journey spanning a period of around five decades and selected aspects of the related developments by others. In addition to writing about the methodological aspects, I have also discussed some broader implications of the thermobarometric and compositional zoning data of natural samples derived from metamorphic rocks and mantle xenoliths, and further insights that might be gained by analysing these data within the framework of heat transfer relations. In several sections, I included some background information and stories behind the development of my research programmes and ideas, some of which would give a sense to the younger generation that a career in research has ups and downs,



some of the latter being quite heartbreaking; there are also some elements of luck and one also needs to have a collaborative attitude to take advantage of the infusion of ideas from unanticipated directions.

Although I have spent almost my entire professional career in the academia, I was not an academically inclined person as a teenager or in my early twenties. I have reminisced about how I drifted to an academic profession and began to enjoy research and how I became a geologist. Through these reminiscences, I intended to convey some sense of time in India and the USA in the later part of the 20th century from the point of view of a young international student and later a member of the academic community in a western society that is, in many senses, far removed from the environment of my upbringing.

For someone who was born in India when it was a subject nation under the British rule, the career choice was often, if not primarily, made by earning potential and that stood in the way of choosing an academic profession. A young man from a middle class family, as I was, was not only expected to support himself, but also his parents and in some cases his extended families to some extent. The Nobel prize winning physicist, Sir C. V. Raman, took the Indian Finance Service (IFS) examination, graduating at the top of the group, and began his professional career as a finance officer in Calcutta or Kolkata, as it is called today. He realised that there was little hope for him to have a career as a physicist with a decent earning potential after he graduated with a Master's degree (M.A) in physics from the Presidency college, Madras, now Chennai¹. Meghnad Saha, who is regarded as a founding father of the field of stellar astrophysics, also wanted to take the IFS examination, following Raman's footsteps, but fortunately for astrophysics, he was disqualified because of his active involvement in India's independence movement. This is the generation of my parents, and although the situation was not nearly as bad in our generation, the family responsibility still played an important role in our career decisions; we were not so free to "follow our nose". Also, for me the academic career did not seem so interesting because of what I saw of the profession; it was, with some exceptions, mostly routine teaching and learning that seemed unexciting.

I am thankful to the Editorial Board of the *Geochemical Perspectives* series for giving me the opportunity to write this article, and grateful to Tim Elliott and Sumit Chakraborty for their reviews and suggestions at different stages of the work in progress that have greatly improved the final product and helped me maintain a focus on the broad objectives of the *Geochemical Perspectives* series. The formal reviews by Bernie Wood and Jim van Orman are greatly appreciated. Eli Bloch helped me refine a portion of the thermochronology section. Jeff Catalano provided me with the reports of the council meeting of the Geochemical Society about 50 years ago that helped me write the story of editorial handling of one of my papers by the executive editor of GCA and the likely consequences

1. Another Nobel prize winning physicist from the same college was Raman's nephew, Subramanyam Chandrasekhar.



in Section 3.2. Hugh Greenwood shared with me his recollection of that episode. Andrew Peart, Alumni News Editor, University of Chicago Magazine, was very helpful in my finding materials from the University Chicago photographic archive and magazine, and Alexei Perchuk, Weiji Cheng and Bernardo Cesare helped me with the captions of Figures 1.6, 1.8 and 2.2, respectively. I also thank Weiji Cheng for his help in the calculation of Figure 5.1. Finally, I am grateful for the meticulous editorial supervision of Marie-Aude Hulshoff, painstaking copyediting by Rob Raiswell who also made excellent suggestions, and the superb graphics work by Juan Diego Rodriguez.

Upon reviewing the article, Bernie Wood commented: “...*It was also a time, the 1970s when experimental petrology and thermodynamics were coming together to tell quantitative stories about rocks and I was reminded of how excited we all were by the rapid advances.*” I hope that the other readers, those who have been through that period and mid-1960s and those who came to the scene afterwards, would also share or get a sense of that excitement.

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ABBREVIATIONS AND SYMBOLS²

Mineral Names

Ab	Albite	Hbl	Hornblende
Act	Actinolite	Hy	Hypersthene
Alm	Almandine	Ilm	Ilmenite
An	Anorthite	Ky	Kyanite
AS	Aluminum silicate	Mt	Magnetite
Bt	Biotite	Ol	Olivine
Chd	Chloritoid	Opx	Orthopyroxene
Cor	Corundum	Opy	Orthopyrope
Cpx	Clinopyroxene	Plag	Plagioclase
Crd/Cd	Cordierite	Pyr/Py	Pyrope
En	Enstatite	Qtz/Q	Quartz
Fsl	Ferrosilite	Sill/Si	Sillimanite
Fo	Forsterite	Spnl/Sp	Spinel
Grt/Ga	Garnet	St	Staurolite
Gr/Grs	Grossular	Ts	Tschermak component

-
2. Since the figures have been reproduced from different sources that did not follow a uniform system of abbreviation of mineral names, several mineral names have two abbreviations. Within the text, I tried to follow the system of abbreviations suggested by Kretz (1983) unless the figures being discussed required otherwise.



Chemical Systems

MAS	MgO-Al ₂ O ₃ -SiO ₂
CMAS	CaO-MAS
FMAS	FeO-MAS
FASHO	FeO-Al ₂ O ₃ -SiO ₂ -H ₂ O-O ₂

Symbols

F	Helmholtz Free Energy
G	Gibbs Free Energy
H	Enthalpy
S	Entropy
D(i)	Diffusion coefficient of the species i
E	Activation energy of diffusion
K _(i)	Equilibrium constant of a reaction (x.i) where x is a section number
K _D (i-j)	Inter-crystalline distribution coefficient of the ions i and j
k _D (i-j)	Intra-crystalline distribution coefficient of the ions i and j
K _X	The compositional segment of an equilibrium constant
K _{is}	A generic equilibrium constant for an isotope exchange reaction
q _i	Molecular partition function of the species i
q _{i::tr} q _{i::r} q _{i::v}	Translational, rotational and vibrational partition functions of the species i
T _p	Peak temperature in a thermal cycle
T _c (i)	Closure temperature of diffusion of the species i in a mineral
q _s and q _m	Surface and mantle heat flux, respectively
H _s	Volumetric heat production rate
a _i /a(i)	Activity of the component i
γ _i /γ(i)	Activity coefficient of the component i
α	Bulk isotopic fractionation factor between two phases
η	A cooling time constant for linear decrease of 1/T(K) vs. time
h	Planck constant (6.62607(10 ⁻³⁴) J s)
k _B	Boltzmann constant (1.38065(10 ⁻²³) J K ⁻¹)
R	Gas constant (8.314 J/mol-K)



ACADEMIC REMINISCENCES AND THERMODYNAMICS- KINETICS OF THERMO- BAROMETRY-CHRONOLOGY

ABSTRACT

This article has three major components that include, in addition to the technical aspects, reminiscences of my academic upbringing, my move to the USA from India, and my professional career. I have recounted many stories that I hope convey some sense of time, especially in these two countries with vastly different cultures, my personal journey with its ups and downs and how I made the transition to an academic career path in USA even though that was not in my future plan as a young man.

The development of the field of thermobarometry and its integration with diffusion and crystal kinetic modelling of compositional zoning (or lack thereof) and cation ordering in minerals have led to important quantitative constraints on the pressure-temperature-time evolution of terrestrial rocks and meteorites. I review the historical developments in these areas and a segment of my own research spanning the period of 1964-2021. The foundational works of the thermometry of metamorphic rocks and palaeothermometry were laid at the University of Chicago around 1950. Subsequently, the synergetic growth



of thermodynamics and experimental studies in petrology in the 1960s and 1970s, along with the introduction of electron microprobe as a nondestructive analytical tool with micron scale resolution, gave a major boost to the field of thermobarometry. There were also significant new developments in the field of thermodynamics of solid solutions in the petrology community and demonstration from observational data, countering strong scepticism, that the principles of classical thermodynamics were applicable to “complex natural systems”. The section on thermodynamic basis of thermobarometry concludes with a discussion of the thermodynamics of trace element and single mineral thermometry.

I further deal with the experimental protocols, along with selected examples, for phase equilibrium studies that provide the bedrock foundation for the field of thermobarometry based on elemental compositions of coexisting minerals in a rock. It is followed by an account of the controversies and international meetings relating to the aluminum silicate and peridotite phase diagrams that play crucial roles in the thermobarometry of metamorphic rocks and mantle xenoliths, respectively. The construction of quantitative petrogenetic grids to display stability relations of minerals in multicomponent–multiphase systems came into play in the field of metamorphic petrology in the mid-1960s and early 1970s. Augmented by experimental data, these petrogenetic grids led to important discoveries about the P-T- $f(\text{O}_2)$ and bulk compositional controls on the stability of certain “index” minerals that are used to define metamorphic isograds and different types of regional metamorphism; one such grid also opened up a new field that came to be known as ultra-high temperature metamorphism. The construction of petrogenetic grids has now evolved to computer based calculations of complex equilibrium P-T phase diagrams, commonly referred to as “pseudosections”, by minimisation of Gibbs free energy of a system with fixed bulk composition. I discuss these historical developments and modern advancements. Subsequently I highlight some aspects of thermobarometry and diffusion kinetic modelling of selected natural samples along with their broader implications and present a critical discussion of different protocols for thermobarometry of natural assemblages.

Following up on the introductory historical perspective of development of palaeothermometry, I discuss the modern advancements using density functional theory (DFT). Examples of DFT based calculations have been shown for hydrogen isotope fractionation in mineral-water/hydrogen systems and “clumped isotope” thermometry. The hydrogen isotope fractionation data led the development of new low temperature palaeothermometers using serpentine-talc/brucite mineral pairs. These results enable simultaneous solutions of both temperature and source of fluid in the serpentinisation process of rocks.

The final section is devoted to high temperature thermochronology dealing with the problems of closure temperature of decay systems in minerals and the use of bulk and spatial resetting of mineral age according to a specific decay system to determine cooling rates of the host rocks. Complications arise in the interpretation of mineral ages determined by such decay systems as ^{176}Lu - ^{176}Hf or



the short-lived system ^{53}Mn - ^{53}Cr in which the parent nuclide has a much lower closure temperature than the corresponding daughter product. Numerical simulations help explain the discrepancy between the ^{176}Lu - ^{176}Hf and ^{147}Sm - ^{143}Nd ages of garnets in metamorphic rocks and enable construction of the entire T-t cycle from the discrepant ages and some additional constraints.



1.1 Becoming a Geologist

As one entered college in Kolkata, the city where I was born and raised, one had to make a choice between the two streams, science (Intermediate Science: I.Sc.) and arts (Intermediate Arts: I.A.). I went for the science stream, and at this point one of my uncles suggested that I should choose geology as my optional subject (physics, chemistry and mathematics were the required ones) because he had heard that the Indian Government was going to hire a lot of geologists to work at the Geological Survey of India and other Government organisations under its five year plan. The primary objective of this large scale hiring of geologists was exploration of India's natural resources that would help it to transform to an industrialised society in the post-independence period. Even though I knew nothing about geology, I followed my uncle's advice. As we began our college career, the field work related to geology became a major attraction to many of us as they involved visits to new and scenic places, far away from the city life, and, of course, family supervision. Also, in these field trips I first got the taste of some creative thinking. It was a satisfying departure from the routine task of reading what is in the book and answering questions in the examinations related to those materials; things like working out a structure or a stratigraphic correlation seemed quite interesting to me.

After successful completion of the I.Sc. examination, we were faced with the hard task of deciding on a subject, from those studied earlier, to be the honours subject for the Bachelor of Science (B.Sc.) programme. The honours programme was, however, not open to all students. One could usually move forward to the Master of Science (M.Sc.) programme, which was my goal, only in the subject in which one held a B.Sc. (honours) degree. I chose Geology as my honours subject primarily because of its job potential and also because I had developed some liking for it. I went on to obtain a M.Sc. degree in Geology from the Jadavpur University (JU), Kolkata. The course work in a two -year Master's programme was completely restricted to the chosen field and was the same for all students. This was not such a well thought out educational programme, not only in JU but also in many other places India; it did not properly recognise the inter-relationship among different scientific disciplines and special interest and talents of the students within a given discipline (*e.g.*, petrology *vs.* palaeontology). (Linus Pauling is said to have once commented that a chemist who always thinks about chemistry is not a good chemist; whether he actually said it or not, I cannot agree with it more.) During the course of the M.Sc. programme, structural geology became my favourite subject, which was probably because of its quantitative nature that matched my natural inclination and also because we had an outstanding professor, late Prof. Subir Ghosh who later became an internationally reputed figure, to teach the subject. Thus, I did a M.Sc. thesis focused primarily



on structural field mapping in the area around the Udaipur City, Rajasthan, and petrofabric analyses of deformation induced twinning lamellae of plagioclase in a granite pluton (Gangopadhyay¹, 1961).

1.2 Atomic Energy Establishment (India) and “Coming to America”²

After getting my M.Sc. degree I accepted an offer for a position of Scientific Officer in the Metallurgy Division of the Atomic Energy Establishment (AEE), Bombay (now known as Mumbai) that was later renamed as the Bhabha Atomic Research Centre (BARC) after its founding father and distinguished physicist, Homi Jahangir Bhabha³. It was as good a job – well paid and secure – that a young person with a Master’s degree and just out of college could have expected to find in India at that time. It was then a common practice of the Government that all applicants who satisfied the minimum required qualification for a job, as advertised, were to be called to appear for interview for the job, with the travel expenses being paid by the Government. Thus, this was a great opportunity for those of us, who performed well in the examinations, for Government paid sight- seeing trips! The trip to the Mumbai, erstwhile Bombay, from Kolkata by a group of recent graduates that included myself was initially planned as one of those trips; we were all waiting for the advertisement from the Government of India for a large number of positions in the Geological Survey, which was our first choice, to come out soon, and take some of these sightseeing trips in the meanwhile. However, when the official offer came from AEE, which to me was made verbally right after the interview, it turned out to be too good to decline but I remember that I was somewhat upset because it meant that I would have to leave my comfort zone of family and friends in Kolkata and get adjusted to living by myself in a different cultural and social environment. (India is a multi-lingual – 23 official languages with Hindi and English being the two most spoken ones – and a multi-cultural country with large variations in the food habits of the local people in different parts of the country; it is probably more homogeneous now than it was when I went to Mumbai.) However, after I got to Mumbai, I became quickly adjusted, and started enjoying my freedom from family supervision, and landed through an acquaintance, who was a movie actor and whom I knew very well, within a group of young Bengalis who had migrated to the film capital of India – now commonly referred to as Bollywood – from Kolkata to try their luck and talent in the movie industry. Some of them later became Bollywood movie

1. Ganguly is a shorter version of the last name Gangopadhyay; also see Section 1.3 about the meaning and abbreviations of the Bengali last names.

2. “Coming to America” is a famous song by Neil Diamond.

3. Bhabha was a highly acclaimed theoretical Physicist from the Cambridge University where he also did a degree in mechanical engineering and mathematics (trips); see Leslie and Chowdhury (2018) for Bhabha’s role in the development of India’s nuclear programme.



director, cameramen and actor. So much did I hang out with this group and learn their jargon that I was once mistaken as an aspiring person in the movie industry already on a successful track!

When I joined AEE, it was still in a formative stage and had collaborative programmes with organisations in the western world, especially USA, for training of the new recruits. Also, many stalwart physicists from the western world, who were Bhabha's good friends, came to AEE to teach short courses. I was told that I would be among the group to visit for a year the Argonne National Lab in Chicago; this was to take place near the end of my first year of service. I was quite excited about the prospect of visiting USA; I had never been abroad before and that added to my excitement as well. However, to my great disappointment I did not get selected presumably because there were other people who joined AEE before me and had been in the queue longer – seniority of service had an important role in the selection process (this preference for seniority also permeated the promotion process in Government and University jobs.)

My boss sensed my disappointment and mentioned to me that I should be able to get admitted to a graduate programme in a good University in USA, if I applied on my own. And if I chose to take that route, then it should be quite possible for me to take a study leave and return to AEE after successful completion of an advanced degree. I followed his advice, eventually accepted an offer of a fellowship from the Department of Geophysical Sciences of the University of Chicago, and sailed by boat from Mumbai on September 3, 1962, gazing at the receding shoreline with teary eyes as the Italian boat, Roma, slowly departed from Mumbai harbour; I knew that it would not be until after I had finished my degree that I would have a chance to return to India. My application for study leave was declined for technical reasons but I was given hopeful indications of a serious consideration if I chose to apply to AEE after finishing my degree at Chicago. I had no doubt in my mind that immediately after completion of my degree, I would be back to the same building (Engineering Hall No. 4) of AEE. However, I have never visited that building again although I very much wanted to and still do!

Before sailing, I bought a copy of the book by Hans Ramberg (1952) on "*Origin of Metamorphic and Metasomatic Rocks*" for reading on the boat when I had nothing better to do during the long voyage. I think that the book was suggested to me by Prof. Sisir Sen, who did his Ph.D. under Ramberg at Chicago and joined the faculty of the newly founded Department of Geology and Geophysics in the Indian Institute of Technology (IIT) at Kharagpur (~2 hours by train/car from Kolkata) a few years ago. This book has a 70 page chapter on "*Thermodynamics of Metamorphic Processes*" that gave me my first exposure to the subject of thermodynamics and its potential to tackle petrological problems in a quantitative fashion but without demanding too much of mathematical knowledge. I still have that book (more about this book in Section 2.2.1), and I am not aware of any other writing on thermodynamics at that time of comparable pedagogical value to geologists.



A memorable event in the long journey by boat was an after-dinner dance and music performance on the upper deck of the boat by the troupe of the famous Indian dancer, Uday Shankar (elder brother of the great sitar maestro, Ravi Shankar), under a full moon sky when the African coast became visible. Uday Shankar and his troupe were going on a tour of Europe and USA, and they put on this performance at the request of the captain of the boat, who was persuaded by some of us in the Indian group to make that request.

Using a combination of (a) train from Kolkata to Mumbai across the width of India, (b) boat from Mumbai to Genoa, Italy, *via* a bus ride from Cairo to Alexandria through the Sahara – my first view of a desert that was awe inspiring – and a visit to the pyramids, (c) train once again from Genoa to London that involved crossing of the English channel by a boat, (d) plane from London to New York (my first plane ride); and finally (Greyhound) bus, I arrived at the International House of the University of Chicago (Fig. 1.1) on September 21, 1962, after around three weeks of journey and with almost no money. India gained independence only 15 years previously from the British colonial rule and was struggling with a foreign exchange crisis that was, however, not the only crisis. As a result, a student going abroad for higher studies was permitted to convert a very limited amount of Indian currency to a foreign currency, and only if the University that he/she was admitted to was included in an outdated list of reputable institutions. I had just enough money to survive for a few days and had to take a loan from the University almost immediately after my arrival.



Figure 1.1

The International House, University of Chicago (1414 E. 59th Street), meant primarily for the accommodation of foreign graduate students and international scholars. Credit: University of Chicago Photographic Archive, [digital item number: apf2-04374], Special Collections Research Center, University of Chicago Library.



1.3 Chicago Days: The Formative Period

A massive complex of two multi-story buildings with imposing gothic style architecture, the International House, or the I-house as it is usually called (Fig. 1.1), was a wonderful place for the accommodation of foreign graduate students and visiting scholars. Within a couple of days, I met a young post-doctoral fellow, Mihir Chowdhury (deceased) who also arrived from Kolkata a few days previously after a couple of years as a post-doc at Penn State. His specialties were quantum chemistry and spectroscopy, but he also had a very good grasp of practically all areas of physical chemistry; he played an important role in my learning of the subject, developing my liking for it and survival in the graduate programme at Chicago. Besides the social interaction with students from many different countries and exposure to different cultures, a most attractive aspect of life in the I-house was the large array of expertise available within the graduate student and visiting scholar population that made it much easier for us to deal with homework assignments and also to get additional helps in courses outside of our own disciplines (*e.g.*, mathematics and physical chemistry for me) than someone living in an apartment⁴.

At Chicago, I faced a problem with my name almost immediately after my arrival. My full name, which was used in all my official documents such as passport, degree certificates, application forms for admission *etc.* is Jibamitra Gangopadhyay. I quickly realised that both my first and last names are quite difficult for the western tongue. The “padhyay” segment of the last name comes from Upadhyay, which means teacher; it is also associated with some other last names of people belonging to the Bengali Brahmin caste, such as Mukhopadhyay, Bandopadhyay *etc.* that got transformed to anglicised forms of Mukherjee, Banerjee *etc.* during the British rule of India. The shorter version of Gangopadhyay is Ganguly, but it is debated if it is an anglicised transformation or not. At any rate, I told everyone that I may be addressed as Ganguly. It did not occur to me that I that I could have told them to address me as Jiba, as I am addressed today by friends and colleagues. The reason for this is that addressing someone by first name beyond a certain stage of acquaintance had been a rather uncommon practice in India (and the students addressing their professors by their first names was, and still is, a punishable offense!). Thus, most of my Chicago professors

4. Sometime ago, the administration of the University of Chicago made a decision to partly or completely tear down the I-house and construct a building with modern facilities to satisfy the needs of the present generation of students. There was an outcry against this decision, especially among those who lived there as foreign students and scholars. I wrote a letter to the president – I am sure that many others also did so – explaining what the I-house meant to the foreign students/scholars and demolishing it would trigger a very unfavourable reaction among that group. I got a personal response from the President explaining why the decision was made, but the project never took off; I guess that some facilities were modernised instead of large scale tearing down or reconstruction.



addressed me as Ganguly and the practice continues. But when my wife and I took American citizenship, we officially changed our last names to Ganguly⁵ which has been used in all my publications except the first one.

I came to Chicago without any assigned adviser – such a situation was quite common those days, at least at the University of Chicago (UC) – but after some discussion with me about my interest, the graduate student adviser, John Jamieson, told me that Bob Mueller, who had just joined the faculty of Geophysical Sciences as an Assistant Professor, would be an appropriate adviser for me, at least initially. (When I applied to Chicago, I wanted to work with Hans Ramberg, but he left before I arrived there, accepting a position at the University of Uppsala, Sweden.) Bob Mueller, Ralph Kretz and Sisir Sen belonged to the same group of Ramberg students and Sisir Sen had already made Mueller aware of me. However, Jamieson did not feel that I had the thermodynamics background that was needed to work with Mueller or even to take his petrology courses, and thus gave me a list of physical chemistry courses that I needed to take, along with some mathematics courses to go along. Jamieson was a physicist and thus emphasised quantitative studies in fundamental sciences for the graduate students. I had some anxiety initially since I never studied physical chemistry before and my mathematics was rusty as there was very little use of it in the two years of M.Sc. programme in Geology in India; however, eventually I ended up taking even more courses in physical chemistry and mathematics. At the UC, Bob Clayton, then an Associate Professor of Chemistry and Geophysical Sciences, taught a course entitled “Physico-chemical principles” that was meant to be a physical chemistry primer for the graduate students in the department of Geophysical Sciences. This course was a wonderful starter for me in the realm of physical chemistry.

After I felt adequately prepared in thermodynamics through Clayton’s course and the first quarter of the physical chemistry series in the senior undergraduate level in the Chemistry department, I took Mueller’s advanced petrology classes. The course was loosely structured, and the emphasis was on showing applications of thermodynamics and, to some extent kinetics, to petrological problems. There was no book at that time to adequately complement Mueller’s course material. However, Mueller recommended that we read the book on Chemical Thermodynamics by Prigogine⁶ and Defay as much as we could and also Ramberg’s book. The material covered in the two courses by Mueller constitutes a substantial part of the book by Mueller and Saxena (1977) entitled “*Chemical Petrology: with applications to the terrestrial planets and meteorites*”.

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5. The last name Ganguly may ring a bell in the ears of the Cricket fans in the former British colonies. When my younger son, Sujoy (Fig. 1.5), went to the Cambridge University for his graduate studies and started spelling his name in the check-in counter of his College, the person in the counter quipped when Sujoy came to his last name: OK, I know how to spell that one. A superstar of the Indian cricket team around that time was Sourav Ganguly, who also led the Indian squad to the world cup final a few years earlier.
 6. Ilya Prigogine, who later won the Nobel Prize in Chemistry, then had a joint appointment with the University of Chicago and the University of Brussels.



For the final examination of one of his courses, Mueller walked in and said: *Well, I prepared some questions for you for the exam; however, yesterday I read that the data sent by the atmospheric probe launched by the Soviet Union to Venus showed that its atmosphere is mostly composed of CO₂ and its temperature is ~500 K.* Additionally, Mueller remarked that since the mass and density of Venus are comparable to those of the Earth, it would be reasonable to assume that the two planets have roughly the same bulk composition (he might have given some more hints – at this distance of time I am unable to recall). So, Mueller asked: with these data, what can you tell about the crustal mineralogy/petrology of Venus? He gave us several days to work on this problem as a take home final examination. We were initially shell shocked, but ultimately managed to come up with some reasonable answers.

The main thing that Mueller was looking for was whether we could catch on, based on our experience and knowledge about natural rocks, to the implication of the high atmospheric temperature in terms of facilitating equilibration between the CO₂-rich atmosphere and the Venusian crust (with Earth-like bulk composition) and thus come up with something about the nature of the crustal mineralogy. Here my familiarity with carbonate rocks and Bowen's decarbonation series through my geology training in India was helpful, but I also went on to speculate that the basaltic rocks would very likely display a calc-alkaline differentiation trend if the high P(O₂) condition in the atmosphere had some effect on that in the magma chamber. I made this suggestion based on what we learned in Mueller's class about the work of Muan and Osborn on the effect of P(O₂) on the crystallisation-differentiation trends of basaltic magma (Muan and Osborn, 1956; Osborn, 1959)⁷. This experience in the second semester of my graduate student career in the USA made a strong impression on me about the distinction between knowledge acquisition (the Indian experience) and creative thinking utilising the acquired knowledge⁸.

While writing this article, I recalled that I had read in an issue of *The University of Chicago Magazine* that a physics student in the Enrico Fermi era (early 1950s) was told by his adviser that he had two problems to work on for his Ph.D. degree: the first problem was to find a problem and the second one was to solve it. I forgot the names of both the student and the adviser, as well as the year of publication of the magazine, but this professor-student interaction has stuck in my mind as it somewhat also reflected the environment in Chicago when I was a student. However, with the prompt help of the Alumni News Editor of the

7. Mueller (1969a) was later dismissive of Osborn's idea on the origin of calc-alkaline differentiation trend in terrestrial basalts.

8. Later Mueller published several papers on atmospheric chemistry and crustal petrology and rheology of Venus (e.g., Mueller, 1963, 1964, 1969b). Some of his predictions did not turn out to be correct as he did not consider some stable atmospheric species in his calculations, but, as emphasised by Lewis and Prinn (1984, p. 150), "*Mueller's basic rationale for the assumption of strong atmosphere-lithosphere interaction has, however, remained unchanged and has served as the basis for all subsequent work*".



magazine, Andrew Peart, I found out that the student was John Goodenough who, at the age of 97, shared the 2019 Nobel prize in Chemistry for the discovery and development of the lithium ion battery, and the adviser was the famous solid state physicist Clarence Zener (Zener diode, Zener effect) (the article was written by Gregg, 2016).

For my Ph.D. research, Bob Mueller made some suggestions but did not spend much time thinking about what I should do. Once after some discussion, he told me that *“one day you come with something that I am surprised, and then you get your degree”*. I tinkered with a couple of problems, one was field based and the other was about the stability of the garnet group of minerals about which very little was known at that time. I finally wrote the proposal for the dissertation research on the latter. One of my foci in that proposal was to find a good explanation of why garnet was found to change composition as a function of metamorphic grade. The work would have required some moderately high pressure experimental studies, and the only such facility available at Chicago at that time was what was known as “Simple Squeezers” in the laboratory of Julian Goldsmith (anyone heard of these devices? I typed the name in Google but nothing showed up, but this was an apparatus designed by Griggs and Kennedy (1956) for high pressure experiments that eventually gave way to the piston-cylinder apparatus in the development of which George Kennedy also played a major role). A typical set up consisted of two opposing anvils between which a sample was placed and surrounded by a gasket to prevent its extrusion; this assembly was enclosed within a split furnace connected to a temperature controller. I did some experiments with this “pre-historic” apparatus and managed to synthesise quite large translucent crystals of almandine-pyrope solid solution from a glass starting material mixed with a sodium fluorosilicate (Na_2SiF_6) flux in the powdered form.

In 1963-64 the Department of Geophysical Sciences appointed two new Assistant Professors, Bob Newton and Bob Berner. Newton, who did his Ph.D. at UCLA under George Kennedy, started setting up a high pressure piston-cylinder lab, which was probably the fourth such labs in the world at that time, the three others being at UCLA, Northwestern University (in the Metallurgy department) and the Geophysical lab. Newton, then a bachelor living in the I-house (Fig. 1.1), and I used to go to dinner together quite often at the basement cafeteria of the University Hospital (Billings Hospital), which was close to our department. As a graduate student, I could not afford anything fancier and Newton, although not constrained by his earnings, did not see the need for anything fancier (he has a Gandhian lifestyle and never even took any summer salary from his many research grants⁹ throughout his career so that he had more funding available

9. In the US academic system, non-administrative faculty members are usually paid by the University for the academic year of nine months, and they are eligible to pay themselves up to three months from research grants; the summer salary is a typical component of research grants and in the numerous research proposals that I have reviewed so far, I have never seen any that did not contain a component of summer salary in the budget unless the investigator had the eligible summer salary already covered by other grants.



for his research). We used to have many discussions over dinner, often around petrology, and my Ph.D. dissertation topic evolved through these (basement cafeteria) dinner meetings. Newton offered to train me in high P-T experimental techniques in the piston-cylinder apparatus in his lab (Fig. 1.2) and thus my dissertation research took off in a focused track leading to a thesis on the stability relations of chloritoid and staurolite as function of P, T and $f(\text{O}_2)$ (Gangopadhyay, 1967) (only a small number of mineral stabilities were known at that time). However, garnet never left me. (I recently re-read my Ph.D. research proposal on garnet – yes, I still have an ammonia printed copy! – and found the influence of the thought and research that went into writing that proposal in my papers on the solid solution properties of the garnet group of minerals: Ganguly and Kennedy, 1974; Ganguly, 1976)

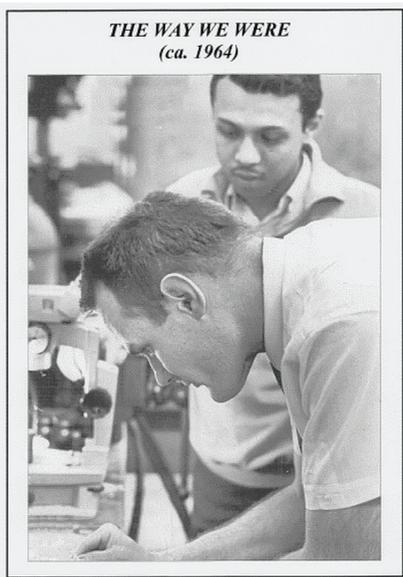


Figure 1.2 Bob Newton demonstrating an experimental procedure to the author in his high-pressure laboratory.

During the course of my dissertation research, Newton became my effective adviser and taught me many things on one-on-one basis in petrology and high pressure experimental techniques that became my bread-and-butter asset as I moved on to an academic career later. Being the only graduate student in his lab, I probably got much more attention from Newton than the large number of students and post-docs that followed as he became an international star. And yes, Mueller was indeed “surprised” by what I produced in the end. I was truly



fortunate to have a brilliant theoretician (Mueller) and an experimentalist of the highest order (Newton), both with keen eyes on the real world, as my advisers; my Ph.D. dissertation and subsequent research reflect this dual influence.

As my dissertation research progressed, Bob Newton heard that Ole Kleppa in the Chemistry Department was developing a calorimeter with which one might be able to determine the enthalpies of solution of rock forming minerals using lead borate solvent. This turned out to be a breakthrough in the calorimetric studies of rock forming minerals. A very fruitful collaboration quickly developed between Newton and Kleppa, with Newton providing the know-how for synthesising minerals of desired compositions along with identifying the petrologically important problems, Kleppa providing that for the calorimetric measurements of heats of solutions, and both joining forces in the interpretation of the calorimetric data— the rest is history.

After I managed to synthesise Fe end members of staurolite, chloritoid and garnet – not an easy accomplishment at that time – and came up with a rough idea of the P-T stability of staurolite, I submitted a paper, co-authored with Newton, for the 1965 GSA meeting in Kansas City. In time I, Fred Anderson and a couple of others headed for Kansas City by train from Chicago. I think that I prepared some handwritten transparencies, but I also planned on writing on a chalk board several things for my talk (all papers were selected for oral presentation at that time). It was my first scientific meeting, and I had no idea what such a meeting was like. When I attended the meeting well ahead of my talk, I found that there was no chalk board in the room. So, I asked for one. People were a bit surprised, but no one was annoyed, and a chalk board was hauled into the room during a break. After my talk, I felt quite embarrassed about my naiveté, but Fred assured me, perhaps seeing how embarrassed I was, that the talk indeed went quite well. And perhaps it did since I was asked to repeat the talk after I returned to Chicago, but this time I had the luxury of a typical wall mounted large classroom chalk board and around half an hour to give the talk.

The Department of Geophysical Sciences started having informal colloquia, mostly around the research that was going on in the department and sometimes featuring talks by visitors from outside (some professional colleague passing by or visiting Chicago). It was in one of these that I repeated my GSA talk. In one such seminar, Kleppa walked in with a female graduate student, who looked more like a beginning undergraduate, from the Chemistry department to introduce her to the world of Earth Scientists. The student – the only woman in the room – was Alex Navrotsky, who by now has received almost every award and honour that there is to receive in the field of Earth Sciences. There was also a weekly after dinner informal seminar at the Fermi Institute that I attended occasionally when the titles of the talks were not too incomprehensible or there was a stalwart figure or a friend or someone from my department giving the talk. Many Chicago luminaries used to be present in the talks. In every talk that I attended, I found a professor in the audience – most likely the famous nuclear chemist Professor



Anthony Turkevich, if my memory serves me right at this distance of time – who had the habit of falling asleep (or closing his eyes) after 10-15 minutes into the talk but waking up in time to ask a question, quite often the first one!

One may now appreciate the thermodynamics and more broadly the physical chemistry power that existed in the Department of Geophysical Sciences of the University of Chicago in the 1960s: Bob Mueller, Bob Berner, Bob Newton, Bob Clayton and Ole Kleppa (the last two holding joint appointments with the Chemistry department). Besides Bob Newton, the experimental petrology programme also had two other stalwarts, the departmental chair and Bowen's student, Julian Goldsmith and Peter Wyllie, who arrived about a year before I graduated. Goldsmith (Fig. 1.3) did not teach us any course as he was too busy with his administrative responsibilities – the department was going through a major transition and reorganisation after the merger of Geology and Atmospheric Sciences programmes – but was always available for advice and was full of good humour. (This merger led to the Department of Geophysical Sciences to which I was admitted and was probably the first such merger in the history). Following is a quote from what I wrote in the Newsletter (December, 1999) of the UC Department of Geophysical Sciences in the section on "In Memory of Julian Goldsmith": *"But in spite of his heavy administrative duties, we used to see him in the lab very often doing his experiments and reading his X-ray data (from films). it seemed to me that he had to do some experiments by himself to be in a good mood for the day"*¹⁰.



Figure 1.3 Julian Goldsmith (1918-1999) with Bob Newton (left) at the retirement party of Newton at the University of Chicago in 1993.

10. There are several pieces in that issue about Julian Goldsmith, including a full page moving poem by Goldsmith's close friend, Gerry Wasserburg, that are worth reading.



The academic administrators at that time at the University of Chicago were highly distinguished academics, with George Beadle (Fig. 1.4), the Nobel Prize winning geneticist as the president (he also taught an introductory course on genetics, as far as I remember). The president's quarter is close to the I-house and on weekends, we would often see Beadle working on his garden or fixing something around the house, dressed up like a handyman with tools hanging from a belt.



Figure 1.4 George Beadle (1903-1989), left, who became president of the University of Chicago less than three years after receiving the Nobel Prize in 1958 for his landmark contribution to Genetics, with biochemist Arthur Kornberg (1918-2007; Nobel Prize: 1959) at the University of Pennsylvania when they were awarded honorary degrees in 1964. Credit: University of Chicago Photographic Archive, [digital item number, e.g., apf1-00412], Special Collections Research Center, University of Chicago Library.

During my stay at Chicago, Ian Carmichael came over as a visiting scientist from England. He was a classically trained igneous petrologist and had very little knowledge of thermodynamics. However, he got interested in learning it while he was at Chicago; the environment almost demanded it. Later, after moving to the University of California, Berkeley, he emerged as a leading player in the field of application of thermodynamics to igneous petrology and produced a stellar group of students who took over and dominated the field. The Carmichael school may be the most influential one in the field of igneous petrology.



The first electron microprobe in USA was set up by J. V. Smith around 1964 at the University of Chicago in a room adjacent to the one that housed the main analytical tool in the department at that time, a large Jarrell-Ash spectrograph, which I and some others learned to use as part of the lab component of Mueller's petrology class. The data for the element fractionation in coexisting minerals in the pioneering works of Kretz (1959) and Mueller (1961) that I have discussed in the Section 2.2.1 were collected using this spectrograph.

The arrival of the electron microprobe became a game changer. We came to know about non-destructive spot analysis of minerals and that minerals often show compositional variations within a single grain. But it was not clear, at least to me, what to make of the latter aspect. Then came a talk by a post-doc from Ed Anders group in the Fermi Institute by the name of John Wood, who was to become one of the foremost figures in the field of meteorite studies and planetary science. He presented data on the compositional variation across the exsolution lamellae in metals in meteorites, as determined in the electron microprobe in the UC, and showed how these data could be used to deduce the cooling rates of the samples and thereby constrain the size of their parent bodies. I still remember that after the talk I told Mueller that finally someone showed what to do with the microprobe data on the compositional variation within single grains.

The work of Wood (Wood, 1964, 1965) and another contemporary study of exsolution features in iron meteorites by Goldstein and Ogilvie (1964) gave birth to the field of what is now known as "metallographic cooling rates" that have since been refined by many workers and extensively applied to deduce parent body structure, size and processes. I discuss in Section 2.4 the transition of geothermometry to geospeedometry through diffusion kinetic modelling of grain scale compositional variations in minerals; the above studies of iron meteorites represent the first applications of diffusion kinetic modelling to deduce cooling rates of natural samples, and was nearly twenty years ahead of such studies within the terrestrial community.

Of the many talks by visitors from outside, one talk is especially worth recollecting. It was by Bob Dietz, a totally unknown person to the students, and the topic was something like Sea Floor Spreading; it was sometime in 1965. None of us, at least the students, had any idea of what it meant. I remember that after the talk people were quite uneasy and some whispering comments in the audience were not complimentary. Many years later, sometime in the late 1980s, when I was going to the Lunar and Planetary Science meeting in Houston, I was reading something during the flight that attracted the attention of the elderly gentleman seated beside me. He asked me if I was going to LPSC – he could tell that by looking at the stuff that I was skimming through. After I said yes, the gentleman told me that he was also going to LPSC and introduced himself as Bob Dietz!! I was quite excited to meet one of the founders of the Plate Tectonic theory and told him that long ago I attended his talk on Sea Floor Spreading at the University of Chicago when I was a graduate student there. He smiled and told me that he remembered the talk and also the audience reaction!



At Chicago, Bob Berner wanted to teach a graduate level course on low temperature geochemistry – this was to be the first course that he taught in his illustrious career– and even though my interests were in high temperature processes, I was told to take that course as it would augment my knowledge of thermodynamics. I registered for the course and it turned out that I was the only one to do so, but in Chicago that was enough for a course to be taught¹¹. There were, however, many auditors in the class (in the US academic system, an auditor is someone who attends a class but does not get any grade for it in his/her transcript). The recommended textbook was Garrels (1960): *Mineral Equilibria at Low Temperature and Pressure* (Garrels was Berner's adviser), but the scope of the course material was much more than that covered in the book by Garrels. Since I was the only student, I thought Berner would give me a grade based on my performance in the homework assignments and not give me a regular final examination, but he did. I got a B in the course, but after reviewing my graded paper, I felt that I deserved an A. So, when I kind of meekly expressed my dissatisfaction for not getting an A, Berner cut me off and said: “No, A means perfect, and this is not perfect”! I took my “revenge” by not taking the follow up course in the next quarter, and as a result Berner was unable to teach the course, but I later regretted very much that immature decision. For many years Berner mentioned me as “my first guinea pig” (however, see Section 2.3.3 for a more complimentary label that I had later acquired).

Before concluding my Chicago chapter, I would like to add a couple of my academic experiences related to the Ph.D. comprehensive examination¹² in 1964 and some incidental accounts relating to thermodynamics. For the written part, I dropped by in Mueller's office to know if he would suggest something that I should focus on (this is not an uncommon practice among the graduate students appearing for the comprehensive examination in Earth Sciences as it is not a formalised subject like other branches of science). Mueller asked me if I knew anything about thermodynamics in a gravitational field and my response was an unequivocal no. He then said something like: *OK, I didn't expect that*

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11. A famous story of a small class in Chicago was that of one taught by Subrahmanyam Chandrasekhar to a group of just two students, Yang and Lee, both of whom later went on to receive the Nobel Prize in Physics. However, an emphatic NO, Berner did not teach the class because he felt that I was so bright, but because he wanted to teach it and it appeared to Mueller and him that I might be one of the few students who could survive the onslaught of thermodynamics.
 12. In US education system, a candidate for a Ph.D. degree is required to take a set of courses before starting the dissertation research so that he or she has acquired a fairly high level of knowledge in the chosen and supporting fields. The comprehensive examination is supposed to test what it says, *i.e.* the level of comprehension of the subject matter and in addition the ability for creative thinking utilising the acquired knowledge. If a candidate does not pass this examination in two chances, he/she gets dropped out of the Ph.D. programme and often leaves the department with a Master's degree.



you would know; so, read a paper by Brewar (1951) on this subject in the Journal of Geology – you know enough thermodynamics to understand that paper. I will ask you a question on this topic.

I went through the paper very carefully, deriving every equation that there is in the paper, and went to Mueller one day to ask a question about something that I was having some trouble with (I do not remember what it was). Mueller listened to me and said: *OK, I give you a ‘pass’ since I find that you have gone through the topic very carefully, understood it quite well and are thinking about it.* One may see the impression of that learning process during the Ph.D. comprehensive examination in Ganguly (2005) and in my book on thermodynamics. In the first edition of the book (Ganguly, 2008), I derived a relation for the change of isotopic ratio with height in a gravitational field that was subsequently verified by the data in a static sedimentary column (shown in Section 8.16 of the second edition in 2020, Section 8.16). Failure to account for the effect of changing height in a gravitational field on the thermodynamic potentials invalidated the quantitative results of a thought provoking Nature paper by David Waldbaum (1971) on temperature change associated with adiabatic decompression in geological processes. The problem with the paper by Waldbaum, who was a leading thermodynamicist in the Earth Sciences in our generation, was immediately caught by Martin Dodson (1971) and Hans Ramberg (1972). Dodson is known in the Earth Sciences community for his seminal paper (Dodson, 1973) on the problem of closure temperature in geochronological systems – see Section 7.1 – and not for any thermodynamic contribution. I was unaware of Dodson’s paper for a long time, and when my attention to this paper was drawn by one of my former students, Max Tirone, it further lifted my already very high admiration for this “unsung hero” in our field.

During the oral part of the examination, Bob Clayton asked me what I would do, given access to all the money that I needed, to test the recent idea of Ted Ringwood that there might be significant amount of Si in the Earth’s core. Comprehensive examination is a do-or-die stressful situation and I just froze upon getting a question like this. After some silence Bob Mueller asked Clayton: *what would you do?* Clayton responded: *I have no idea, but let’s see if this guy can think of something* (I did very well in Clayton’s course – so, he might have had a good opinion about me that landed me into this trouble).

1.4 Later Years

1.4.1 Yale University

Bob Berner soon became a rising star and was lured away by Yale before the completion of my Ph.D. degree even though he was given an early tenure by the UC, sensing that it might otherwise have difficulty retaining him. When I was nearing completion of writing my dissertation, I went to a GSA meeting where



I met Berner. After some exchanges of “*how are you*” etc. type, he asked me if I would like to come to Yale as a post-doc. And if I did, Berner suggested that I write to Sydney Clark, who was setting up a high pressure piston-cylinder lab and to also ask Clark to talk to him. I followed Berner’s advice, and soon got an offer of a post-doctoral fellowship from Clark (in the letter Clark indicated that he had also contacted Bob Newton). And so, it seemed that in the end it really did not matter that I was not “perfect”.

I joined Yale in January 1967, and there I wrote my first NSF (US National Science Foundation) proposal that was funded in full while Yale University supplemented the funding by returning 37 % of the overhead! I received much research funding later, but it was only once more that I received what was asked for in a proposal. And about getting a return from the overhead money? Yes, I got a fraction of a percent for a very limited period and do not know of anyone who had better luck. The proposal was for the continuation of my research on chloritoid and staurolite stabilities (more on this in Section 4.1). So, with Clark’s help it did not require much effort to write the proposal, as I knew clearly what I wanted to do and the style was quite informal; the entire proposal was thirteen pages long with just one page for the budget of a two year grant. Clark designed the piston-cylinder apparatus and had it fabricated and assembled before I arrived at Yale. I never had it so easy since I had complete freedom in terms of what I wanted to do and the continuation of my post-doctoral research was not contingent upon my generating external funding although I managed to do so.

Yale had a wonderful academic environment and I recall with pleasure my interactions with several other faculty members, especially Phil Orville and Karl Turekian, and several graduate students (John Grover, Larry Grossman, Rosemary Vidale, Dave Hewitt, Don and Sharon Bachinski etc.). The many students and faculty members whose research related to petrology started organising a “Petrology Club” after dinner talk and discussion about once or twice a month in some faculty member’s house. Phil Orville often took over the responsibility of organising the Club meetings. (The students joked about this: Phil would plan everything in meticulous detail including getting the special drinks and munchies for some students that they liked but might forget to select a speaker!) I gave a talk in the Petrology Club on the role of oxygen fugacity on the stability relations of some key metamorphic minerals – a subject matter of my Ph.D. dissertation and ongoing post-doctoral research, and how large differences of $f(\text{O}_2)$ might have persisted within small volumes of metamorphic rocks, borrowing partly on the latter aspect from a paper by Mueller on the mobility of elements in metamorphism (Mueller, 1967a). The talk generated quite a bit of discussion among the group about what might have been responsible for the similar sequence of Barrovian minerals in different metamorphic terranes (I would return to this topic in Section 4.1). The next day, when I was having lunch with my wife in a campus eatery, Phil came in for lunch and sat with us. The first thing that he said to my wife was: *your husband gave an interesting talk yesterday, but we talked more than he did – he got us into a long debate among ourselves.*



1.4.2 Return to India

I came to USA with a very restricted type of visa (J1) that required me to return to India after 18 months of “practical training” beyond my Ph.D. I managed to get a year’s extension for the completion of my work, but that was it! I probably could have managed to stay longer by changing my visa status, which was quite difficult but not impossible, but decided to return to India instead of going through all the hassle for the continuation of my stay in USA. And not only myself, but many Indian students in my generation looked for an opportunity to return to India after completion of graduate studies and post-doctoral research in USA or elsewhere.

I was able to complete most of the planned experimental and theoretical studies for a paper on staurolite stability before leaving for India; the plan was to do the thermodynamic calculations and write the paper after settling down in my hometown, Kolkata. I carried a separate brief case containing whatever I did for this project to avoid the dreadful situation if the checked in baggage got misplaced. My wife and I made a planned sightseeing stop in Rome *en route* to India but while checking in the hotel, I discovered to my horror that I had left the brief case in the airport. I immediately turned around, keeping my wife in the hotel lobby, and took the next bus to the airport holding my breath but with little hope of finding the briefcase. After I arrived at the Da Vinci airport and ran up to the Customs, I found the brief case sitting on the Customs counter. Apparently after going through the Customs, I collected the other checked in bags, but forgot to pick up the briefcase. I told the Customs officer that it was my bag, and he asked me to pick it up, no questions asked!! Had the brief case gotten lost, my career probably would have ended in Rome, being deprived of one of my most important papers – see more about the work in Section 4.1 – at the formative stage of my career.

In India, I was unable to find a faculty position in an Earth Sciences department. There was a sense of discomfort among many people in the power structure in having a young person of my academic background and western exposure around them in the same department. Also, the rigid system and outsized weight given to teaching experience meant that I had to start at the bottom of the ladder, which I refused to do. The idea of trying to return to the Atomic Energy Establishment, by then already renamed as the Bhabha Atomic Research Center, evaporated from my mind; by then I got too hooked up to an academic career and research in Earth Sciences. Finally, I ended up in the Department of Chemistry, Birla Institute of Technology and Science (BITS), Pilani, Rajasthan, to teach physical chemistry, especially thermodynamics.

In BITS I shared an office with another young assistant professor, Bidyendu Deb (known in the professional circle as B. M. Deb), who returned to India after doing his Ph.D. in Oxford with the highly respected theoretical quantum chemist, C. A. Coulson. From Bidyendu, I got my first exposure to the Density Functional Theory (DFT). It was 1971, when DFT was not well known even in the community of physics and chemistry and probably totally unknown in the field



of earth scientists (the theory was developed during the period 1964-65 by the theoretical physicists Walter Kohn, Pierre Hohenberg and Lu Sham; Kohn shared the 1998 Nobel prize in Chemistry with John Pople who developed the computational strategy and algorithm, including implementation of DFT, the latter in a famous software package known as GAUSSIAN – see Section 6.2). I was, thus, one of a very small group of people in Earth Sciences, maybe even the only one, to have an exposure to DFT long before it made its phenomenal impact after the development of the commercial computational quantum chemical software packages implementing DFT. Although I did not pursue any DFT based geochemical study then – I did not quite know what to do with it – but thanks to this initial exposure and the consequent psychological adaptation, I have been able to get involved decades later in collaborative research using DFT, a part of which has been captured in the Section 6.2.1, to deal with problems in mineral physics (e.g., Ottonello *et al.*, 2008, 2010), planetary sciences (Asaduzzaman *et al.*, 2015) and stable isotope fractionation (Asaduzzaman and Ganguly, 2018, 2021).

Life in BITS, Pilani, was turning out to be professionally very stale for me, virtually devoid of any research activity and disconnected to the world of Earth Sciences; there was no one around who could even tell a granite from a sandstone. At this point I received a brief letter from George Kennedy, whom I never met, saying that his former student Bob Newton had told him that I had not been able to do much in terms of research in India and that I might like to return to USA; so, the letter said, come on over any time you want. I was excited to get this offer but also was a little hesitant to accept the invitation as number of people in USA told me that the job market there was very tight. So, I wrote to Kennedy expressing my concern and Kennedy responded by essentially a one liner: *“there is absolutely no shortage of jobs for absolutely first rate persons”* (this was the typical Kennedy style). Many years later I told Alex Navrotsky what Kennedy wrote to me and Alex responded: *“That’s absolutely right”*.

1.4.3 Back to USA: UCLA and the University of Arizona

I finally accepted the timely offer from Kennedy and returned to USA in April 1972, for a second post-doc career in Kennedy’s group. My chloritoid-staurolite series of papers (Ganguly, 1968, 1969, 1972; Ganguly and Newton, 1969) had come out by then and caught a fair amount of attention among metamorphic petrologists. I think that I had a modest level of name recognition by then (two of these papers were later widely discussed in Petrology text books and review articles). Kennedy had practically no knowledge of what I had done and published – a letter from Bob Newton was good enough for him to make me an offer – and so he was a bit surprised when I was invited to give a talk in the departmental colloquium.

After some time during which I worked on melting temperatures of Pb, Zn and U up to almost the highest pressures (>60 kb) achievable in a piston-cylinder apparatus and also determined the phase diagram of propargyl alcohol (!), I met



Julian Goldsmith in an AGU meeting. He inquired about what I was doing in Kennedy's lab. After about a couple of weeks, Kennedy came to my office and told me that he had been on the phone with Julian (they were good friends), who told him to leave me alone for a while. After a little pause to see my reaction, Kennedy said "*OK, do whatever you want*" and left. Thus, finally I got the chance to "follow my nose" at least for a while after a hiatus of around three and half years in the most critical period of my career (more on life with Kennedy in the Section 2.3.2). And it was indeed very difficult to make a comeback to academia.

The post-docs that overlapped with me in Kennedy's group included Susan Kieffer, Anil Singh (a physicist), Reinie Boehler and Peter Mirwald. Considering what each of them has achieved in his or her career path, it was a very impressive group. There was, however, no graduate student. Although the work that I was doing in Kennedy's lab was not to my liking and, frankly, would not have gotten me anywhere if I had continued on that track, I learned during the course of my tenure there and especially from Ivan Getting many techniques and design aspects for doing experiments in a piston-cylinder apparatus up to pressure of ~65+ kb; no group outside of Kennedy's lab has succeeded or even attempted such high pressure experiments in a piston-cylinder apparatus. (Ivan was the central technical figure in Kennedy's operation and the go-to man for all our problems in the lab.) This helped me greatly in developing the high pressure experimental petrology programme at the University of Arizona. These days, experiments above ~35 kb are almost always done in the multi-anvil apparatus in which the sample volume is much smaller and the accuracy in the determination of sample pressure and temperature is poorer compared to that in the piston-cylinder apparatus. (Kennedy and Ringwood in the Australian National University at Canberra were trying to push the limit of piston-cylinder apparatus to ~100 kb. However, the design of the multi-anvil apparatus in Japan became a game changer as it enabled experimental investigation to conditions in the deep interior of the Earth using sample volumes that can be analysed in a microprobe and investigated in an electron microscope.)

From UCLA, I moved to the University of Arizona as an Assistant Professor of Geosciences in 1975 with a startup money that after adjustment for inflation is around one fifth of what is being offered now in our department for a similar hire. From the point of view of my research interests, however, the environment could not have been much better. There were two people, Tim Loomis and Denis Norton, who played especially important roles in the further development of my research and teaching programmes. Also, Mike Drake was in the Planetary Science department and was building a strong programme in Planetary petrology-geochemistry (more on Mike Drake in Section 2.4.1). Tim had already established himself as a leading figure in the field of kinetics of petrological processes, especially diffusion kinetics in multicomponent solid solutions such as garnet, and Denis was a leader in the field of heat and mass transfer as they relate to the full spectrum of fluid-rock interactions, from thermomechanical to chemical. The extraordinary environment of teaching and research in quantitative petrology and geochemistry at the University of Arizona in the 1980s has been



highlighted by Sumit Chakraborty, an alumnus of the University of Arizona and the current president elect of the Geochemical Society, in his acceptance speech for the Dana medal of the Mineralogical Society of America (Chakraborty, 2017).

Both Tim Loomis and Denis Norton also had a smart group of students working on petrological kinetics and heat and mass transfer problems. I found the group to be stimulating in terms of my interest and inclination. Additionally, there were a few smart graduate students who were hanging around for the right person to arrive in the faculty after their adviser, Burt Nordlie, who was my classmate from Chicago, left to accept a position at the Iowa State University. One of these “orphans” drifted to me after I arrived and finished his dissertation research. This student is John Delaney, a famous name in the field of oceanography¹³.

Life at Arizona soon became quite difficult because of the restrictive nature of the visa with which I and my wife had returned to USA and the dogged effort of a local immigration officer to get us deported. *“This guy had his education at our expense and I am not going to let him spend the rest of his life in our country”* was his telephone message to the University representative who was handling my visa problem. But thanks to the Herculean efforts of the department head, Ed McCullough, who managed to get the local congressman, Maurice Udall involved in the process of changing our visa status, we were finally able to beat the process of deportation and gain permanent residence status in USA (Udall was then running for the presidential nomination of the Democratic party against the president to be, Jimmy Carter). The fiercely opposing forces of the society are still at play and no less so than they were about 45 years ago!

Through interactions with Tim, I quickly transitioned to the field of diffusion kinetics and together we developed a programme of experimental and theoretical research in this field and its application to the retrieval of the time scale of petrological processes *via* modelling the compositional zoning in garnet (more on this in the Section 2.4.2). Steve Elphick, who had worked on a field based problem relating to compositional zoning in garnet at the Cambridge University, arrived as a post-doctoral fellow just in time. Although Steve did not have any experience in experimental petrology, he soon turned out to be an excellent experimentalist with clever ideas and played a pivotal role in the development of the technique of diffusion couple experiments at high P-T conditions (a diffusion couple is a pair of crystals with a highly polished interface across which diffusion takes place, smoothing out the compositional discontinuity at the interface).

When we submitted a proposal for funding to NSF, I was told that some reviewers expressed concern about the survival of a diffusion couple without intense fracturing at the pressures (20 to 45 kb) of our proposed experimental

13. John recently visited us and told an interesting story. When his son was visiting India, he saw a huge billboard with a picture of the superstar Indian actor Amitabh Bachchan. He took a picture of the billboard and sent it to John with the comment that Dad, this famous Indian actor looks like you. My wife and I looked at John and indeed were struck to notice the similarity that we never noticed before! Maybe a Bollywood movie career is awaiting him.



studies. The concerns were quite legitimate. Thus, we did a quick experiment with a diffusion couple of olivine; garnet was substituted by olivine since we did not have garnet crystals of the quality (*i.e.* inclusion and fracture free and compositionally homogeneous) that were needed for this type of experiments, but had some olivine crystals of the desired quality. The experiment was successful, and I sent to the programme director a picture of the quenched olivine diffusion couple along with the microprobe data of the induced diffusion profiles across the couple interface. I do not know how the programme director handled the situation (*i.e.* submission of substantive material after the submission of a proposal), but the proposal got funded. The review and funding process was not so formalised at that time, and if it were like it is today, we would have had to wait for one more year for resubmission of the proposal addressing the reviewers' comments, in which case it was quite possible that we would have drifted to some other direction in order to maintain our research "productivity" and funding.

We got lucky in getting funded, but the trouble began when we did an experiment with the garnet-garnet diffusion couple. Garnet is much more brittle than olivine and thus the diffusion couples kept getting quite intensely fractured at the high P-T conditions because of the anvil effect at the interface, exactly as the reviewer had suspected. However, eventually Steve and I were able to come up with a design that involved quite difficult fabrication of the pressure cell and shaping and interface polishing of the diffusion couple that led to success (Elphick *et al.*, 1985). Sumit Chakraborty came on board as a graduate student (Fig 1.5) after Steve accepted a position at the University of Edinburgh, and the programme of multicomponent diffusion kinetic studies of garnet flourished (Chakraborty and Ganguly, 1991, 1992; Ganguly *et al.*, 1998) despite the setback due to Steve's departure and the resignation of Tim Loomis from a tenured faculty position to pursue a different career path away from Earth Sciences.

The diffusion kinetics or more broadly the crystal kinetics programme gradually branched off to other directions (different minerals and problems) with the involvement of new graduate students and senior colleagues. Some of their studies relating to the overall theme of this *Geochemical Perspectives* article have been discussed in different sections. As my research programme progressed in the direction of crystal kinetics, I became interested in the problem of cooling rates of rocks, and, in general, the thermal history of rocks. The first problem that I worked on was the response of the Fe-Mg ordering states of pyroxenes to cooling rates. My continued involvement in this type of research became possible primarily through support from NASA. It was very difficult, and probably still is, to get into the NASA circle. I was told by the programme director that he had "admitted" only two (or something like that) newcomers into the programme in the year that I was trying to secure some funding but was unsuccessful. It sounded quite bizarre to me, but with time I found out that once someone was on board, NASA, unlike NSF, tried to keep that person funded so that he/she could develop a stable programme of planetary research provided, of course, that person continued to submit competitive proposals and published important papers from



the previous cycle(s). I found that policy to be very helpful, especially for someone doing experimental studies. The story of how I managed to get “admitted” into the NASA programme is narrated in the Section 2.4.1.

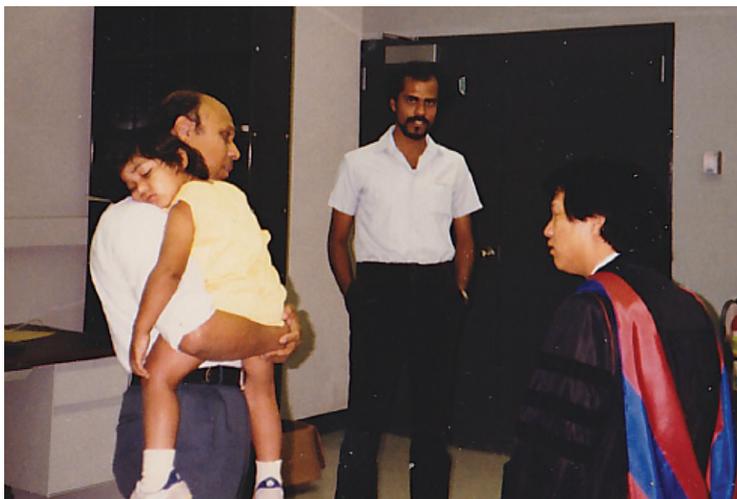


Figure 1.5 The author with a sleeping four-year old (a future Cambridge Ph.D.) and two graduate students in the experimental petrology laboratory following the 1987 convocation in which Han Yang Lee (right) received his Ph.D. degree. The other student is Sumit Chakraborty – the President-elect of the Geochemical Society. The garnet -orthopyroxene geothermometer by Lee and Ganguly (1988), based primarily on Lee’s dissertation research, is a widely used geothermometer for mantle xenoliths and granulites.

One evening in the fall of 1989, I got a call from a gentleman in China, Dr. Weiji Cheng (Fig. 1.8), who identified himself as an Associate Professor of Geology in the University of Science and Technology (UST), Heifei, which is a premier institution in the mainland China. He had worked with Hugh Greenwood before and requested an opportunity to work with me. After talking to Greenwood, I worked out an arrangement for Weiji’s appointment as a visiting associate professor in our department that was to be supported by my research grants. His move to my group and many years of participation in collaborative research was one of the best things that had happened to the further development of my research activities. He co-authored several papers with me, helped new students learn high P-T experimental techniques and also translated the first edition of my book on *Thermodynamics in Earth and Planetary Sciences* into Chinese. Weiji is now settled in Los Angeles with his wife, both as American citizens.



Geochronologists have been determining cooling rates using multiple mineral age data according to different decay systems from the same rock *vs.* the closure temperatures of the decay systems. A closure temperature (T_c) is supposed to be that at which diffusive loss of the daughter nuclide from a mineral grain effectively ceased, thus fixing the zero time of a geochronological clock. (This is the conventional definition of closure temperature of a decay system, but problems arise if the parent nuclide had remained open to diffusive loss/gain after the daughter nuclide closed within a mineral, as discussed in Section 7.3). It has always been my approach, as it certainly is for many others, to spend some time to read and understand some seminal papers whenever I began research in a new direction. For closure temperature, the groundbreaking contribution was by Martin Dodson (Dodson, 1973) that has since been used extensively in all calculations of closure temperatures. I spent quite a bit of time to carefully go through this intensely mathematical paper, and especially the Appendix that contained most of the mathematical details, instead of being satisfied with the final equation for the calculation of T_c given in the Abstract of the paper. In that process I coerced my elder son, Rajib, to explain to me some of the mathematical manoeuvrings in Dodson's paper when he came home for the Christmas break after a grueling first semester at Penn State as a graduate student in Astronomy. I will return to the problem of closure temperature and my interactions with Dodson in Section 7.1; however, at this point it is worth recollecting my first meeting with Dodson that would convey a sense of his personality.

Text box 1.1 – Martin Dodson – The Gentleman Scientist

Dodson and I continued to exchange e-mails for several years, and in 2002, when I planned to attend an IMA (International Mineralogical Association) meeting at Edinburgh, Dodson invited me to come over to Leeds after the meeting so we could chart out a course to work together on some of the problems relating to closure temperature that we had been discussing through e-mails and Fax. I was delighted to have the opportunity to meet Dodson. The plan was that I would get down at the Leeds train station, and my wife would take a train from there to Oldham to visit her cousin. As I was waiting on the platform with my luggage, Dodson showed up, was able to quickly identify me within the crowd ("you looked like a person waiting to be picked up" was his response when I asked him how he recognised me) and immediately asked "*where is your wife?*". My wife was climbing up the stairs carrying a small suitcase to go to the other side of the platform to catch the train to Oldham. Dodson immediately ran up the stairs to help her with the suitcase. He was a true gentleman scientist! During the drive from the station to the University, I found out that Dodson was an accomplished musician (a piano player, if I remember correctly) and used to spend a good chunk of his time with music and performing with a music group. Also, he served as a consultant for some manufacturers of mass spectrometers.



1.4.4 Some international activities and outreach

I like to travel, especially to different countries, and have travelled extensively in connection with international meetings and short courses organised by different groups. I recollect below some of the meetings and short courses that have some special significance to me and may be of interest to the readers.

My first international travel in connection with a meeting was to the Soviet Union for the 11 th IMA meeting in Novosibirsk (Siberia) in 1978 during the period of the cold war, when it was firmly behind what was called the “iron curtain”. I was a part of the American contingent whose travel was supported by the NSF. Every single aspect of our travel had to be decided and paid for before we left USA and the entire logistics had to be handled by a state-run travel agency called Intourist. We had no choice about the hotels that we would have liked to stay; it was decided by Intourist that did not respect our request to be assigned the same hotel so we could hang around as a group of friends. We stayed for a few days in the gorgeous city of Moscow for sightseeing before taking off to Novosibirsk. During the flight, the visitors were made to sit in a section of the plane separated by a curtain from the locals.

In the meeting in Novosibirsk (Fig. 1.6) we were received very cordially, and it seemed that the Soviet scientists were eager to meet those from the other nations, and especially USA, and exchange ideas. During one such discussion, I expressed my admiration for the work of the famous petrologist from the Soviet Union, D. S. Korzhinskii, whose work had influenced my own research (see Section 4.1). The next day the Soviet scientist that I talked to – it was probably Slava Fonarev (Fig. 1.6) – came back with a list of things that Korzhinskii had done wrong, at least according to him, and wanted to discuss his list with me. I did not get the time to sit down for what was likely to have been a lengthy meeting. However, it should be noted that Korzhinskii’s work on the thermodynamics of open systems was hotly debated in both Soviet Union and USA (see, for example, the 1969 presidential address of Jim Thompson to the Geochemical Society; Thompson, 1970). And whether or not this scientist had some valid criticisms of Korzhinskii’s work, I was impressed to see that he was not afraid to express his opinion in an international meeting against the work of a person with the stature of an Academician. Science had managed to maintain the much needed atmosphere of freedom in an otherwise controlled environment that did not even permit contact between the foreigners and locals during a flight.

There were two languages permitted for the presentations of papers in the IMA meeting, English and Russian. This was unlike the custom today with only English, but of all kinds, being the official language for presentations in an international meeting. There were some people engaged in each session of the meeting to translate the talks from one language to the other. While this was going on, in one session I suddenly heard a familiar female voice translating a Russian talk to English, taking over from the official translator. I turned my face



and saw that it was Alex Navrotsky. The translator was not doing a good job, so Alex took over for the rest of the session. Later I came to know that both parents of Alex were Russian immigrants to USA, and she spoke Russian as a child.



Figure 1.6 A group picture with the Soviet scientists and Surendra Saxena during the IMA meeting (1978) at Novosibirsk in the former Soviet Union. From left to right: Vyacheslav (Slava) Fonarev (1937-2007), Surendra Saxena, Nikolay Sobolev, Leonid Perchuk (1933-2009) and the author.

On my way back to USA from the IMA meeting, I visited Prof. Hans Ramberg in Uppsala (Fig. 1.7) and gave a talk at the Geology department. Thus, I finally got a chance to meet the person whom I had greatly admired and with whom I might have worked for my Ph.D. if he had not left Chicago (see Section 2.2.1 about Ramberg's pioneering role in the field of geothermobarometry).

In 1987, I was invited by the Council of Scientific and Industrial Research (CSIR), Government of India, to visit India and give a series of lectures under the sponsorship of a UNESCO programme called TOKTEN (Transfer of Knowhow Through Expatriate Nationals). It was decided that I would spend some of my time at my alma mater, Jadavpur University (JU), Kolkata, where I would teach a short course on the applications of thermodynamics to geological problems, and at the National Geophysical Research Institute (NGRI), Hyderabad. I was not sure about how effective the proposed short courses would turn out to be, but I went along with the idea. I was later told by two attendees of the short course in JU, Somnath Dasgupta and Pulak Sengupta (who now have international recognition for their contributions in the field of metamorphic petrology and are members of the Indian National Science Academy along with other honours), that the course made a strong impact and had influenced their research directions. I have since



taught a number of short courses in different places, but I always wondered if the courses were worth the trouble for the organisers and participants. So, it was satisfying to know that at least one was worth it.



Figure 1.7 Hans Ramberg (center: 1917-1998) with Surendra Saxena (right) and Hans Annersten (left) during the author's visit to Uppsala, Sweden, following the IMA meeting in the Soviet Union in 1978.

At NGRI, I gave a series of lectures, one of which dealt with the inferred P-T conditions of charnockites and granulites in the southern India shield that turned out to be much above the steady state geotherm in the P-T space. This talk immediately triggered collaborative research with the geophysicist Rishi Narain Singh (who later became director of two National Laboratories) on exploring the reason behind the thermal perturbation that was required for the formation of charnockites (Ganguly *et al.*, 1995; also see Section 5.4). It was followed up by more collaborative research, continued exchange of ideas and opinions and my visit to give talks to almost everywhere that Rishi moved from his base at Hyderabad for professional reasons.

In 2002, I was invited by the Chinese Academy of Sciences to visit UST (Fig. 1.8) to give some lectures along with my colleague Weiji Cheng and explore the possibility of developing a collaborative research programme; the invitation also included arrangements for some touristic sightseeing. I gladly accepted the invitation. It turned out to be a very interesting cultural experience and the hospitality was incredible. Two things in the UST campus caught my attention. One was that the daily newspapers were posted on long boards for people to read and I found a lot of people reading them. It seemed to me that newspaper subscription for home delivery was not a common practice. The other was a building with a sign



of Center for Quantum Computing. I had heard from friends in computer science that quantum computing would be the next big revolution in that field, but I did not know of anyone involved with it at that time. I was, thus, greatly surprised to see a centre for such a frontier field in a place where people had been lining up to read newspapers posted on boards and the overall research environment seemed to be mostly in the catching up phase. We know today that China has emerged as a leader in the field of quantum computing.



Figure 1.8 A group picture with the Geosciences faculty members of UST (University of Science and Technology), Haifei, after a 25 plus course sumptuous reception dinner. From left: Yongfei Zhen (Department Head); Daogong Chen (the host); Xiachen Zhi; Taixi Zhou (deceased); the author and his wife, Sucheta; Mrs. Cheng and her husband, Weiwei Cheng; Jiangfeng Chen; Zhichen Peng (deceased). All are/were geochemists or geochronologists except for Prof. Zhou, who was a petrologist.



2.1 Introduction

Thermobarometry has now become one of the central components of petrology and tectonics as it allows one to put quantitative constraints on the pressure-temperature path in the evolutionary history of rocks. The principles of equilibrium thermodynamics constitute the bedrock foundation for the formulation of thermobarometric expressions that are applicable to natural assemblages. Diffusion kinetics, on the other hand, determines the spatial domains over which equilibrium was achieved in a rock, as was recognised very early on by Harker (1932) in his comments about Goldschmidt's application of Phase Rule to metamorphic rocks. Because of its wide ranging applications, the field of thermobarometry has seen intense research activity since the introduction of electron microprobe in the 1960s enabling non-destructive determination of the composition of minerals with high spatial resolution, and development of tools for controlled laboratory experiments. It also was greatly responsible for the introduction of thermodynamics and diffusion kinetics in petrology-geochemistry curricula in many Universities and promotion of research activities in these areas in the geological community.

Essene (1982, 1989) provided exhaustive reviews of the then “current status” of the entire field of thermobarometry and these papers still serve as important documents and a road map for the field. I will not attempt a similar review in this article. Instead, I limit myself to the thermodynamic and kinetic aspects of the methods of retrieval of P-T conditions of rocks on the basis of (a) inter- and intra-crystalline exchange reactions, and (b) construction of petrogenetic grids involving isopleths of mineral compositions and also at fixed bulk compositions. Additionally, by extension of (a), I discuss some methods of retrieval of the time scales of petrological and planetary processes. Selected thermobarometers are discussed only in relation to the history of introduction of specific theoretical concepts and experimental and theoretical procedures for formulation of reliable thermobarometers.

After an account of the early and apparently almost forgotten roots of the field, I discuss the thermodynamic and kinetic aspects of thermobarometry, including their historical developments in each section. At the outset I emphasise that while retrieval of the peak P-T conditions of rocks are often the primary goals of thermobarometric studies, it is the kinetic analysis of the resetting of the thermometers, as well as of mineral ages, in response to changing temperature during cooling that constitutes the main observational data for retrieving cooling history of rocks.



2.2 Early History of Thermobarometry: The Chicago School

2.2.1 The Ramberg School: record in element fractionation

Hans Ramberg (Fig. 1.7) was very likely the first person to recognise (Ramberg, 1944, 1952; Ramberg and De Vore, 1951) that the temperature and pressure conditions of rocks, or different stages thereof, could be retrieved from the compositions of coexisting minerals through the application of the principles of equilibrium thermodynamics. This was at a time when eminent petrologists held out considerable reservations about the applicability of equilibrium thermodynamics to complex geological systems, as reflected, for example, in the following statement of Rosenqvist (1949): “*I do not think that it is correct to apply the equations of Gibbs in a complex system (i.e. rocks).*” One may also recall here the hilarious letter of Bowen to Gilluly about the same time in which Bowen explained that the term “equilibria” does not mean “horse shit” (“*equus = a horse and libria = things liberated or discharged*”) that Bowen felt Gilluly was uttering “at the end of each sentence” of his lecture. Bowen advised Gilluly to consult a chemist so someone of his stature in geological circles “*acquire some familiarity with the exact significance of common terms in collateral sciences.*”

Ramberg’s book on *The Origin of Metamorphic and Metasomatic Rocks* (1952) contains a long section on “*Some Useful Relationships between Temperature and Pressure and Composition of Mixed Crystals in Mineral Assemblages*” where he derived formal thermodynamic relations among these variables but was unable to put them to practical use for the lack of data on the thermodynamic properties of rock forming minerals at that time. Earlier Ramberg and DeVore (1951) published a seminal paper that should be considered, inarguably, as the beginning of the whole field of cation exchange geothermometry. In that paper, the authors introduced the concept of ion exchange reaction between minerals and discussed how the fractionation of Fe^{2+} and Mg between coexisting olivine and orthopyroxene should respond to changing temperature, if equilibrium was achieved and both phases behaved as “ideal mixed crystals” (*i.e.* ideal solid solutions).

Ramberg and DeVore (1951) argued that since both olivine (Ol) and orthopyroxene (Opx) “are known to be ionic crystals in which the exchangeable constituents Fe^{++} and Mg^{++} occur in the same state in both minerals, namely as individual ions”, the Fe-Mg exchange reaction should be written in terms of one mole of the exchangeable ions as:



so that, under the condition of ideal solution behaviour of both minerals, the equilibrium constant of the reaction, $K_{(a)}$, takes the form (as written in their paper)

$$\left(\frac{X}{1-X}\right)^{\text{Opx}} \left(\frac{1-X}{X}\right)^{\text{Ol}} = e^{-\Delta G^0/2RT} = K_{(a)}(P, T) \quad (2.1)$$



(the quotation marks indicate the statements by Ramberg and DeVore (1951)). Here $X = \text{Mg}/(\text{Mg} + \text{Fe})$ and ΔG° is the standard state Gibbs free energy change for the exchange reaction at the P-T of interest, written using the conventional end member components of Mg_2SiO_4 and Fe_2SiO_4 for olivine (thus, $\Delta G^\circ/2$ represents the standard state free energy of the reaction (2.a)). Following common practice, the pure state of all end member components at P-T of interest were chosen as their respective standard states. (The standard state is a troublesome concept for people who are not practitioners of chemical thermodynamics. There is some flexibility in how the standard state of a component is to be chosen. The choice, of course, does not affect the outcome of a thermodynamic analysis if the correct procedure is followed. Despite the potential confusion, this flexibility is retained since a clever choice of standard state could simplify the thermodynamic treatment of a problem.)

Ramberg and DeVore (1951) also showed, using the thermodynamic relation for the pressure dependence of $\ln K$, $\partial \ln K / \partial P = -\Delta V^\circ / RT$, (ΔV° : the volume change of the reaction involving the pure end member components used in the reaction), and available data on the molar volumes, that the equilibrium constant is weakly sensitive to pressure changes (they calculated that $\ln K$ decreases by 0.14 for an increase of pressure from 1 bar to 10 kb at 800 K). This was expected to be a general feature for ion exchange reactions. Thus, the distribution coefficients of such reactions, that is the collection of terms to the left of the first equality of the equation (2.1) for a generic exchange reaction between the phases α and β , came to be known as exchange thermometers. In contrast a geobarometer is defined by a reaction, such as



(acronym: GASP), for which the ΔV° is much larger than that of an exchange reaction. Thus, the equilibrium constant of a reaction of the type (2.b), and hence the ratio (K_X) of mineral compositions raised to their appropriate powers in the expression for the equilibrium constant becomes a sensitive function of pressure compared to the precision of measurement of compositions of the natural samples (for the above example, $K_X = \left(X_{\text{Ca}}^{\text{Grt}} / X_{\text{Ca}}^{\text{Plag}} \right)^3$, assuming "ionic solution model" and effectively pure end member compositions of aluminum silicate and quartz). (The credit for introducing this widely used geobarometer belongs to Ghent, 1976).

The important question that now came up is whether a natural assemblage could be assumed to have achieved equilibrium to some set of P-T conditions that it experienced during its evolutionary history. This issue was addressed by two of Ramberg's students, Ralph Kretz and Robert Mueller. Using a spectrograph as the analytical tool in this pre-electron microprobe age, they carried out systematic studies of the compositional variations of coexisting minerals in amphibolite and granulite facies rocks from Grenville gneiss (Kretz, 1959) and amphibolite facies metamorphosed iron formation from Quebec (Mueller, 1960, 1961). They found that when the mole fraction of a major component in a mineral is plotted against that in another coexisting mineral, e.g., $X_{\text{Mn}}(\text{Grt})$ vs. $X_{\text{Mn}}(\text{Hbl})$, the data



defined smooth lines. Two such plots, which are known as Roozeboom diagrams, from the classic studies of Kretz (1959) and Mueller (1961) are reproduced in Figure 2.1a,b.

Text Box 2.1 – Roozeboom plots as indicators of solid solution properties

Equation (2.1) and its analogues for other types of exchange reactions describe a smooth curve in a Roozeboom plot that is symmetric to the line joining $X_i = 1$ terminal points of the two phases. An asymmetry of the trend line, as in Figure 2.1b, implies non-ideal solution behaviour for one or both phases. The model fit to the data in this figure is based on the thermodynamic relationship between the compositions of the coexisting minerals that incorporate the effect of non-ideal mixing of Fe and Mg in cummingtonite according to the simplest non-ideal model, namely the “regular solution” model (see Section 2.3.2); the mineral actinolite was inferred to have an ideal mixing property of Fe and Mg from the symmetric nature of the Roozeboom plot of $X_{Mg}(Opx)$ vs. $X_{Mg}(Act)$.

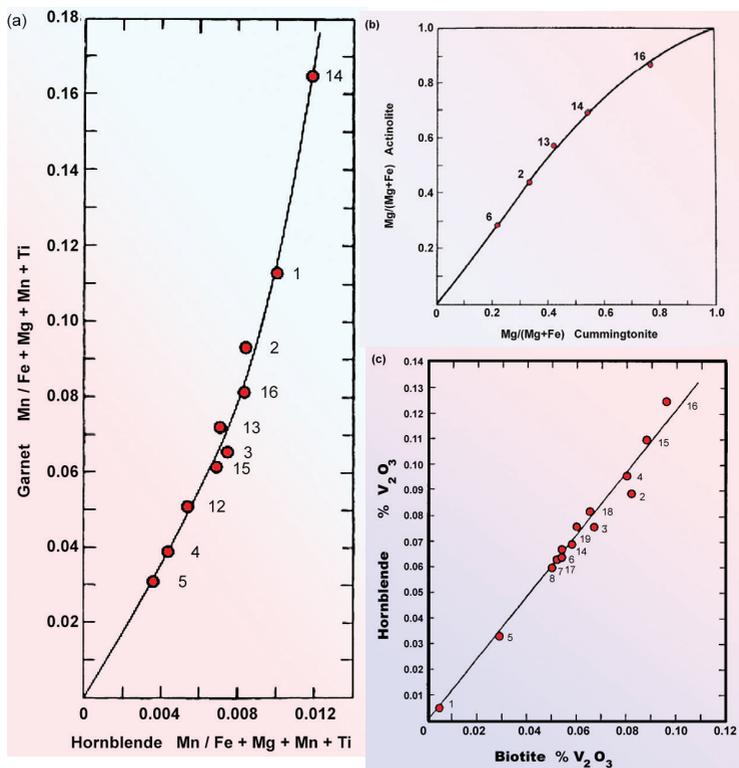


Figure 2.1 Roozeboom plots of (a, b) atomic fractions of elements and (c) wt% V_2O_3 in coexisting minerals. Samples in (a) and (c) are from gneisses in south-western Quebec, Canada, and in (b) from the metamorphosed iron formation, Quebec, in which the solid line is a model fit to the data assuming a regular



solution type behavior and ideal mixing of Mg and Fe in cummingtonite and actinolite, respectively. (a, c) Modified from Kretz (1959). (b) Modified from Mueller (1961).

If one of the species, say i , is very dilute and obeys Henry's law of constancy of the activity coefficient, γ_i , within its compositional range in both phases, then equation (2.1) reduces to the following generic form:

$$\frac{X_i^\alpha}{X_i^\beta} \approx K'(P, T, X_{solv}) \quad (2.2)$$

where α and β refer to the solid phases and $K'(P, T, X_{solv})$ is a constant at a specified pressure, temperature and solvent composition, X_{solv} (as $X_i \rightarrow 0$ and $\gamma_i \rightarrow \text{constant}$, $X_j \rightarrow 1$ and $\gamma_j \rightarrow 1$, according to the Henry's law and Raoult's law, respectively, where j is the solvent component; in the above expression the ratio of γ_i -s of the solute components in the two phases, which is a constant, has been absorbed in the K' term). The above expression may also be written in a formally similar fashion by using wt. % ratio of the species i . Equation (2.2) or its equivalent using wt. %, is known as the *Nernst distribution law*. Thus, a Roozeboom plot of the dilute species i (obeying Henry's law) should define a line with constant slope and zero intercept. Figure 2.1c, which is reproduced from Kretz (1959), shows that the Nernst distribution law is indeed obeyed by the relationship between wt.% V_2O_5 in hornblende and biotite from the Grenville gneiss. Several other examples of adherence to the Nernst distribution law may be found in Kretz (1959).

The pioneering works of Kretz and Mueller inspired a number of subsequent studies of element distribution in co-existing minerals in natural assemblages during the 1960s (e.g., Phinney, 1963; Hounslow and Moore, 1967; Saxena, 1968; Sen and Chakraborty, 1968). The important conclusion that emerged from these studies is that the data on compositional variations of coexisting minerals at temperatures as low as those of medium grade metamorphic rocks conform to the orderly forms in Roozeboom plots that are expected from equilibrium thermodynamics. This insight and the introduction of electron microprobe in the 1960s enabling rapid and non-destructive determination of mineral compositions with micron scale resolution provided the impetus for the subsequent experimental and theoretical studies for the calibration of thermobarometers that are applicable to wide range of natural assemblages.

In the late 1950s, Subrata Ghose (Fig. 2.2), who was a contemporary of Kretz and Mueller at the University of Chicago, began to study the intra-crystalline distribution of Fe and Mg in silicates by X-ray diffraction, at the suggestion of Hans Ramberg (Ghose, personal communication). Intra-crystalline distribution or ordering of cations in rock forming silicates was studied by Whittaker (1949) and Morimoto *et al.* (1960), and since by a number of other workers. However, it was the synergistic activity between Ghose (Ghose, 1961, 1962) and Mueller

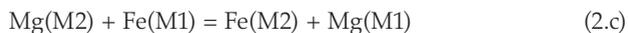


(1962, 1967b, 1969c) that seems to have provided the major stimulation for the development of the field of thermodynamics and kinetics of cation ordering in rock forming silicates. Ghose (1982) provided a comprehensive review of the field covering the crystal chemical details that are responsible for the atomic forces governing intra-crystalline distributions of Fe and Mg in rock forming silicates, and the experimental techniques commonly utilised to determine their site occupancies. A comprehensive review of the thermodynamics and kinetics of Fe-Mg order-disorder in minerals and their applications to petrological problems may be found in a companion paper by Ganguly (1982a).



Figure 2.2 A picture following a splendid music concert in the duomo during the IMA meeting in Pisa, Italy (1994). From right to left: Subrata Ghose (1932-2015), Giulio Ottonello, (wide-eyed) Giulio Jr. and Bernardo Cesare talking to Richard Spiess.

The thermodynamics of intra-crystalline distribution of ions may be treated in an analogous fashion as the inter-crystalline distribution by writing an exchange reaction between the different crystallographic sites, such as



for the fractionation of Fe²⁺ and Mg between the non-equivalent octahedral sites, M1 and M2, in orthopyroxene. However, geothermometers based on this type of exchange reaction are very prone to resetting in slowly cooled rocks because it requires atomic movement at the Ångstrom scale within a mineral to respond to changing temperature. We return to this topic in Section 2.4.1.

2.2.2 The Urey Group: record in stable isotope fractionation

About the same time as the work of Ramberg, Harold Urey developed the idea of a palaeothermometer on the basis of oxygen isotope exchange equilibrium between calcite and ocean water and formulated the expressions of the equilibrium constants of the reactions in terms of **partition functions** in statistical thermodynamics (Urey, 1947). This seminal study provided the early impetus for the design and development of mass spectrometers, the precision of which has now reached an awe inspiring state, and marked the birth of the field of stable isotope geochemistry and thermometry. It is interesting to note that both Urey and Ramberg were at the University of Chicago, in the departments of Chemistry and Geology, respectively, when they laid the foundation of the fields of Palaeothermometry and Geothermometry.

Text Box 2.2 – Partition function

When subject to the constraints of conservation energy and the total number of particles, N , the most probable fraction of particles in a quantised energy state, ϵ_i , within a system of non-interacting particles is given by the Boltzmann distribution law, which is as follows.

$$\frac{N_i}{N} = \frac{\alpha_i e^{-\epsilon_i/k_B T}}{\sum_i \alpha_i e^{-\epsilon_i/k_B T}} \quad (2.3)$$

Here N_i is the number of particles in the state ϵ_i and k_B is the Boltzmann constant; the factor α_i stands for the degeneracy of state i (*i.e.* the number of states with energy). The summation term in the denominator is called the partition function and holds the key to the development of relations between macroscopic (*i.e.* thermodynamic) and microscopic properties of a substance.

For all practical purposes, the equilibrium constant, K , of an isotopic exchange reaction, written in terms of exchange of one mole of isotopes between the compounds (*e.g.*, $C^{18}O + \frac{1}{2} C^{16}O_2 \leftrightarrow C^{16}O + \frac{1}{2} C^{18}O_2$), may be expressed at low pressure in the same form as equation (2.1) with ΔG° being replaced by the standard state Helmholtz free energy change, ΔF° . This replacement is due the fact that the volume change of an isotopic exchange reaction is very small so that at low pressure the term $\exp(-P\Delta V^\circ/RT)$ that accounts for the pressure effect on



K is close to unity at temperatures of geological interest (recall that $\Delta G^\circ = \Delta F^\circ + P\Delta V^\circ$). Using the relationship between F and partition function, one finally obtains

$$K_{is}(1,T) = \prod (q_i)^{\nu_i} \quad (2.4)$$

where K_{is} is the equilibrium constant of an isotopic exchange reaction, \prod is a product symbol, ν_i is the stoichiometric coefficient of a species involved in the balanced reaction (>0 for product and <0 for the reactant compound), and q_i is a molecular partition function. If the rotational and vibrational motions are decoupled, then the latter can be expressed as a product of translational ($q_{i:tr}$) rotational ($q_{i:r}$) and vibrational ($q_{i:v}$) partition functions relating to the quantised energy states of the specific types of motions.

Text Box 2.3 – Harmonic approximation and simplifications

Assuming that the vibrational motions behave as harmonic oscillators (*i.e.* restoring force is proportional to the displacement) and are also decoupled from the rotational motions, Urey (1947) showed that the calculation of K_{is} can be greatly simplified, bypassing the need for calculation of $q_{i:tr}$, $q_{i:r}$ and $q_{i:v}$ separately. This was done by using a method known as the Teller-Redlich product rule; it led to an expression of K_{is} that can be evaluated only from a knowledge of the vibrational frequencies of the species, plus or minus the symmetry numbers. (A symmetry number represents the number of discrete repetitions of the same molecular configuration upon 360° rotation about the symmetry axes of a compound. In the expression of equilibrium constant in terms of partition functions, the symmetry numbers of the compounds cancels out if the light and heavy isotopes are completely exchanged (*e.g.*, $C^{18}O + \frac{1}{2} C^{16}O_2 \rightleftharpoons C^{16}O + \frac{1}{2} C^{18}O_2$)). Traditionally the vibrational frequencies have been derived from spectroscopic data, but in Section 6.2 I will discuss the modern advances towards calculation of the vibrational frequencies using the density functional theory. (A systematic but elementary presentation of statistical thermodynamics with applications to stable isotope fractionation may be found in Ganguly, 2020).

Urey (1947) went on to calculate the equilibrium constant for oxygen isotope (^{18}O and ^{16}O) exchange reactions between a number of phases as function of temperature. Subsequently, he and his collaborators (Urey *et al.*, 1951) applied the calculated K_{is} vs. T relation between calcite and water to the oxygen isotopic fractionation data between a Jurassic belemnite from the Isle of Skye, Scotland, and ocean water that they had determined using a newly developed mass spectrometer. Assuming that the $^{18}O/^{16}O$ ratio of the ocean water did not change with time, Urey *et al.* (1951) showed, on the basis of the data for the samples drilled along an axis of the fossil, that the mean summer and winter temperatures over the life span of the belemnite (three summers and four winters) about 100 million years ago were, respectively, 21 and 15 °C (Fig. 2.3). This landmark study marked the beginning of the field of palaeoclimate research and it also stands out as the first study that addressed the problem of diffusive resetting of an exchange thermometer that I discuss in Section 2.4.



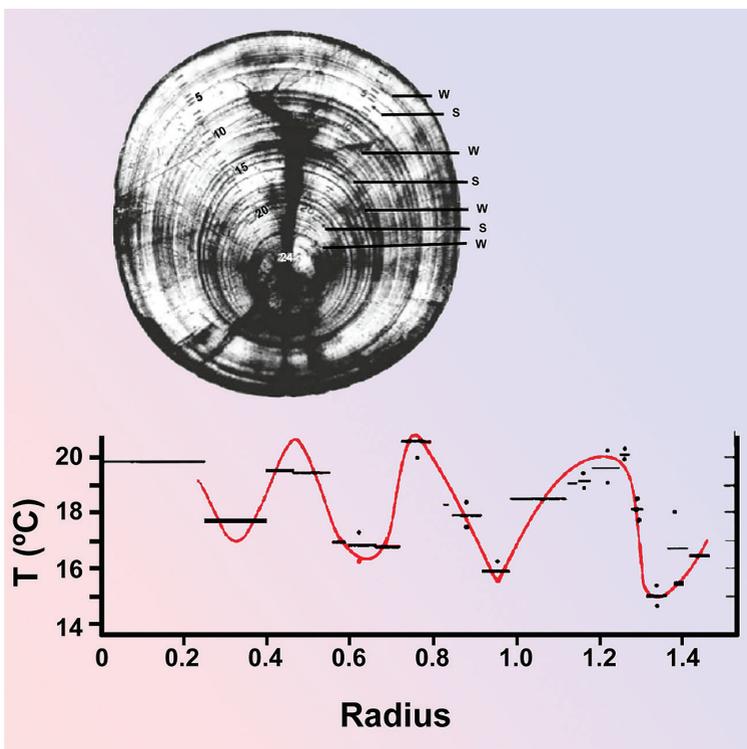


Figure 2.3 A Jurassic belemnite (2.5 cm in diameter) from the Isle of Skye, Scotland, along with the paleotemperatures recorded by the oxygen isotopic ($^{18}\text{O}/^{16}\text{O}$) composition of calcite as a function of radial distance. Modified from Urey *et al.* (1951).

Urey's theoretical work on oxygen isotope fractionation was followed up in Chicago by his student Samuel Epstein and Epstein's student from Caltech, Robert Clayton (and his group) leading to experimental calibrations of $^{18}\text{O}/^{16}\text{O}$ fractionation as function of temperature between many phases of geological interest. An important finding of Clayton and Epstein (1961) was that, unlike element exchange between solids in which $\ln K$ *vs.* $1/T$ is linear over a significant temperature range, for oxygen isotope exchange it is $\ln K$ *vs.* $1/T^2$ that is linear. The former behaviour is easy to understand from equation (2.1) that leads to $\ln K = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R$, where ΔH° and ΔS° are, respectively, the standard state enthalpy and entropy change of the reaction (again to recollect, we have chosen the pure state of an end member component at the P and T of interest as its standard state). For usual solid state reactions that do not involve isotopes, both ΔH° and ΔS° remain effectively constant for a change of temperature of few

hundred degrees and this makes $\ln K$ a linear function of $1/T$ within a bounded temperature interval. However, this is not the case for isotopic exchange reaction. I return to the problem of stable isotope fractionation in the Section 6.

2.3 Thermodynamics of Thermobarometry

2.3.1 General relations

In a generic form, a distribution coefficient (*i.e.* the collection of compositional terms on the left of the first equality in equation (2.1) for a generic exchange reaction), is often written as $K_D(i-j)$ where i and j are the exchangeable species between two phases. It should be easy to see that for an exchange reaction of the type in equation (2.a), $K_D(i,j)$ may be recast in the form $K_D(i-j) = (i/j)^\alpha / (i'/j')^\beta$ where i/j stands for molar or weight % ratios. Analogous collection of compositional terms in the expression of equilibrium constant for a reaction involving decomposition and growth of phases, such as in the GASP reaction (2,b), has been denoted above by K_X . In general, the equilibrium constant $K(P, T) = K_D(\text{or } K_X)(K_\gamma)$, where K_γ is the appropriate collection of the activity coefficient terms in the expression of equilibrium constant in a stoichiometrically balanced reaction. Thus,

$$\ln K_D(P, T, X) = \ln K(P, T) - \ln K_\gamma(P, T, X) \quad (2.5)$$

If all phases behave as ideal solutions, then $K_\gamma = 1$, in which case K_D equals the equilibrium constant and hence depends only on P and T . In other words, if $K_\gamma = 1$, there is a unique relation between P and T for a fixed value of K_D . This is, however, rarely the case, and in general, K_D (or K_X) is a function of P , T and X (*i.e.* the composition of the phases). Accounting for the compositional effect on K_D or K_X constitutes a central problem in the field of thermobarometry. Analysis of this effect through explicit formulation of the $\ln K_\gamma$ term requires an understanding of the thermodynamics of solid solutions. In what follows, I discuss different stages of “transfer of knowledge” in the field of solution thermodynamics from physical chemistry and engineering to mineralogy-petrology, related primarily to thermobarometric studies, and also the significant new advances of general importance made in the latter field.

2.3.2 Thermodynamics of solutions and applications to thermobarometry

The treatment of Ramberg and DeVore (1951) implicitly introduced what is now known as the “ionic solution model” (*e.g.*, Ganguly and Saxena, 1987; Ganguly, 2020), in which a molecular species is assumed to have been dissociated into the smallest ionic units that enable charge balanced substitutions. In this model, the activity (a) of an end member component in a solution of the type $(A, B \dots)_nQ$ is expressed as

$$a_{A,nQ} = (X_A)^n (\gamma_A)^n \quad (2.6)$$



where γ_A is the activity coefficient of the end member component involving one mole of A (*i.e.* $AQ_{1/n}$). The species A, B *etc.* may be single ionic species (*e.g.*, Mg^{2+} , Fe^{2+}) or ionic complexes (*e.g.*, $(NaSi)^{5+}$, $(CaAl)^{5+}$ as in a plagioclase solid solution). It should be easy to see that if the stoichiometrically balanced Mg-Fe exchange reaction between olivine and orthopyroxene is written in terms of the conventional end member formulae (*i.e.* Mg_2SiO_4 , $MgSiO_3$ *etc.*), and the activities of the end member components are expressed according to above relation, then one would recover the relation (equation 2.1) derived by Ramberg and DeVore (1951) if it is assumed that the divalent cations mix ideally. From a purely thermodynamic point of view it is, of course, permissible to write

$$a_{A_nQ} = (X_{A_nQ})(\gamma_{A_nQ}) \quad (2.7)$$

but in that case the behaviour of γ_{A_nQ} would be more complex (*i.e.* non-ideal) than that of the component involving one mole of the exchangeable ion (see, for example, Wones and Eugster, 1965). In the ionic solution model, $\gamma_{A_nQ} = (X_A)^n$ as $X_A \rightarrow 1$, in accordance with the Raoult's law (*e.g.*, Ganguly, 2020).

Text Box 2.4 – Experimental and theoretical support for the “ionic solution model”

Prior to the study of Ramberg and DeVore (1951), Bowen and Schairer (1935) treated olivine as an ideal “molecular solution” of the conventional end member components in the thermodynamic treatment of their experimental data on the melting relation in the forsterite (Mg_2SiO_4) – fayalite (Fe_2SiO_4) join. They were able to successfully model the experimental data by using the thermodynamic relation between melting temperature and composition of an ideal *non-electrolyte* solution, that is by treating $a_{Mg_2SiO_4} = X_{Mg_2SiO_4} = X_{Mg}$ instead of $a_{Mg_2SiO_4} = (X_{Mg})^2$ instead of that follows from equation (2.6). Bowen and Schairer (1935) found good agreement with the experimental data using an enthalpy of melting, ΔH_{mv} value of 14,000 cal/mol (58576 J/mol) for both forsterite and fayalite. Later Bradley (1962) argued that it is very unlikely for the two end members to have the same ΔH_{mv} , considering the large difference between their melting temperatures, and pointed out that Orr (1953) determined the ΔH_m of fayalite to be 22,000 cal/mol (92,048 J/mol). The latter value was, however, found to be comparable to that (25,200 cal/mol = 105,437 J/mol) derived by Bradley (1962) from the experimental data of Bowen and Schairer (1935) by treating olivine as ideal *ionic* solution, according to equation (2.6), of the conventional end member components (the retrieved ΔH_m for forsterite is 29,300 cal/mol). This agreement between the observed and calculated heats of fusion constituted an important step in the acceptance of ionic solution model. The ionic solution model later found support from statistical thermodynamics (Kerrick and Darken, 1975; Ganguly and Saxena, 1987).

With respect to the formal expressions of the activity coefficient term of a species, I discuss only the *regular* and *sub-regular* (also known as the *Margules*) models that have found wide applications in the field of thermobarometry. Comprehensive discussion of different types of solution models may be found in Ganguly (2001, 2020) and Lanari and Duysterhoeft (2019).



In published literature, the model fit to the Fe-Mg distribution data between actinolite and cummingtonite (Fig. 2.1b) by Mueller (1961) in terms of the regular solution model seems to be the first thermodynamic analysis of the non-ideal solution behaviour of a mineral. For a binary solution, the activity coefficient of a component in this mixing model is expressed according to

$$RT \ln \gamma_i = W_{ij}^G (1 - X_i)^2 \quad (2.8)$$

where W_{ij}^G , which is a constant at fixed P-T condition, represents an energetic interaction parameter between the species i and j that relates to the excess Gibbs free energy of mixing according to the symmetric form $\Delta G^{xs} = W_{ij}^G X_i(1 - X_i)$. In a comprehensive presentation of mixing models that may be applicable to simple types of binary solid solutions in mineralogical systems, Thompson (1967) introduced the *sub-regular* or *Margules* model. In this model, the term W_{ij} in the above equation is expressed as a weighted average of two interaction parameters, $W_{ij}^G = \widehat{W}_{ij}^G X_j + \widehat{W}_{ij}^G X_i$ where the \widehat{W}^G terms are constant at a fixed P-T condition and may be decomposed into enthalpic, entropic and volumetric terms, following the scheme of decomposition of Gibbs free energy. It is easy to see that a binary sub-regular formulation reduces to a corresponding regular solution form when $\widehat{W}_{ij} = \widehat{W}_{ji}$. The sub-regular model was, however, widely used in the physical chemistry and metallurgical literature long before its introduction to Earth Sciences.

Ternary extension of the sub-regular model was developed by Wohl (1946, 1953) in the chemical engineering literature from which the ternary regular solution model follows as a special case ($\widehat{W}_{ij} = \widehat{W}_{ji}$). In a ternary solution, there are not only W_{ij} -type interaction terms for the three bounding binaries, but also higher order terms that are usually neglected. A ternary regular solution model that is the same as Wohl's model but without any higher order term was developed independently by Prigogine and Defay (1954) and extended to four component systems by Ganguly (1972). Mixing models for four or more components with sub-regular binaries have been developed by number of workers; all these models are essentially extensions of Wohl's formulation for ternary solution to higher order systems. Cheng and Ganguly (1994) presented a comprehensive review and analyses of these models and showed that all higher order extensions of Wohl's sub-regular formulation of ternary solution are equivalent.

Helffrich and Wood (1989) derived a quaternary solution model with sub-regular binaries in which they showed that such a solution does not contain a quaternary interaction term. This important conclusion was later confirmed independently by Mukhopadhyay *et al.* (1993) and Cheng and Ganguly (1994); the latter also presented an approximate method of estimation of the ternary interaction term(s) from the binary values. Additionally, Cheng and Ganguly (1994) showed that if the binaries have sub-regular mixing properties, then Wohl's formulation is equivalent to two other widely used multicomponent mixing models, namely the Redlich-Kister and Muggianu models that have been very popular in the chemical engineering and metallurgical studies. The multicomponent sub-regular models have been incorporated into the computer programmes of Holdaway (2000) and



Ganguly *et al.* (1996: <https://www.geo.arizona.edu/~ganguly/pub/>) for a variety of thermobarometric calculations involving continuous (or exchange) and discontinuous reactions (*e.g.*, GASP).

For multi-site substitutions, Mueller (1962) suggested an expression for the ideal part of the activity of a component in terms of a product of the atomic fractions of its constituent ions in each site, with each atomic fraction raised to a power that equals the stoichiometric number of the site in the chosen formula unit of the compound. Subsequently, following a lead by Saxena and Ghose (1971) for the disordered orthopyroxene solid solution ${}^{\text{M}2}(\text{Fe,Mg}){}^{\text{M}1}(\text{Fe,Mg})\text{Si}_2\text{O}_6$, Mueller (1972) proposed to account for the non-ideal mixing effect by incorporating activity coefficients that leads to the following expression for a two site solid solution like garnet ${}^{\text{VIII}}(\text{Fe, Mg}, \dots){}^{\text{VI}}(\text{Al, Cr}, \dots)_2\text{Si}_3\text{O}_{12}$.

$$a_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}} = [{}^{\text{VIII}}(X_{\text{Fe}^{2+}}\gamma_{\text{Fe}^{2+}})^3][{}^{\text{VI}}(X_{\text{Al}^{3+}}\gamma_{\text{Al}^{3+}})^2], \quad (2.9)$$

where the γ -s represent site or “partial” activity coefficients of the specified ions in their respective sites.

The expression proposed by Saxena and Ghose (1971) for the activity of a component in the orthopyroxene solid solution is formally similar as the above for almandine, with the sites being M2 and M1. The “ideal” version of their expression (*i.e.* $a(\text{Mg}_2\text{Si}_2\text{O}_6) = {}^{\text{M}2}(X_{\text{Mg}})^{\text{M}1}(X_{\text{Mg}})$ or $a(\text{MgSiO}_3) = [{}^{\text{M}2}(X_{\text{Mg}})]^{1/2} [{}^{\text{M}1}(X_{\text{Mg}})]^{1/2}$) has become widely popular in the thermobarometric literature for the activities of the iron and magnesium end members in orthopyroxene (the source seems to have been forgotten). However, it should be noted that this ideal two site model of the activity expressions for the end member components in orthopyroxene implies negative deviation from ideality while these components are known to have a nearly ideal or a small positive deviation from ideal mixing property. Figure 2.4 illustrates this point by showing the behaviour of the ratio $a(\text{MSiO}_3)/X(\text{MSiO}_3) = \gamma(\text{MSiO}_3)$, where M is either Mg^{2+} or Fe^{2+} , as a function of $X(\text{FeSiO}_3)$ at 600 °C and 800 °C, $a(\text{MSiO}_3)$ being the activity calculated according to the ideal two site model (*i.e.* $a(\text{MSiO}_3) = [({}^{\text{M}1}X_{\text{N}})({}^{\text{M}2}X_{\text{N}})]^{1/2}$). The site occupancies were calculated from the experimental data of Stimpfl *et al.* (1999) and the bulk FeSiO_3 was calculated from the site occupancy data according to $X(\text{FeSiO}_3) = \frac{1}{2}[({}^{\text{M}1}X_{\text{Fe}}) + ({}^{\text{M}2}X_{\text{Fe}})]$.

For geothermometry, activity expression in terms of site occupancies suffers from the practical problem of having to know the temperature for the calculation of the site occupancies. Of course, this problem may be handled iteratively, but the formulation of a geothermometric expression would suffer from the errors of the calibration of intra-crystalline fractionation as a function of temperature. For the above reasons, I prefer activity-composition relations for pyroxenes in the form $\alpha_{\text{Mg}_n\text{Si}_r\text{O}_{3n}} \approx (X_{\text{Mg}})^n$ to the extent that all components could be written in terms of MNO_3 formula units.



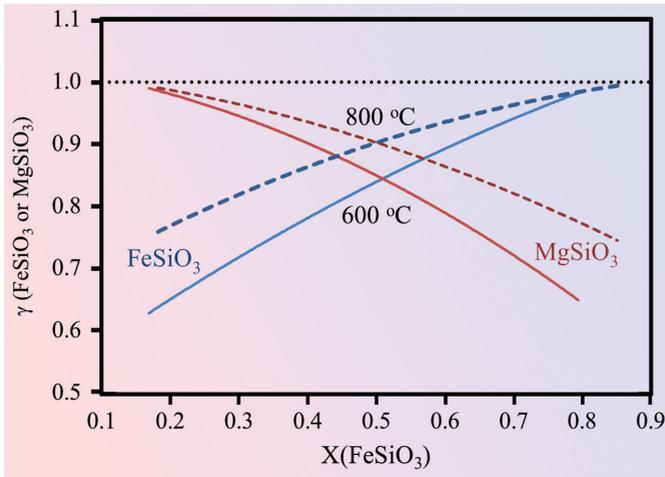


Figure 2.4 The ratio (γ) of the activity of FeSiO_3 and MgSiO_3 components of orthopyroxene, calculated according to ideal two-site model, and the corresponding bulk mole fraction vs. $X(\text{FeSiO}_3)$ at 1 bar, 600 °C (solid line) and 800 °C (dashed line).

In an exchange equilibrium, such as the Fe-Mg exchange between garnet and biotite, the site activity terms like $[{}^{\text{VI}}(X_{\text{Al}^{3+}}Y_{\text{Al}^{3+}})^2]$ in garnet cancel out in the expression of the equilibrium constant since it appears for the activity expressions of both almandine and pyrope that are involved in two sides of the reaction. Thus, the expression of $\ln K_{\text{D}}$ would formally be the same regardless of substitutions in the sites other than those occupied by the exchangeable ions in the two minerals. However, this formal similarity hides the fact that the chemical potential (μ) of a component such as almandine, $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, in garnet depends not only on the substitution in the eight coordinated (dodecahedral) site but also in all other sites (e.g., Cr^{3+} substitution for Al in the octahedral site). While this problem was recognised by several workers (e.g., Kretz, 1961), Wood and Nicholls (1978) were the first to address it formally in the mineralogical-petrological literature on the basis of what is known as the *reciprocal solution model*, which was developed by Flood *et al.* (1954) and Blander (1964) for the thermodynamic analysis of the properties of fused salts. This solution model is also implied in the expressions of chemical potentials of $\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{Fe}_2\text{Si}_2\text{O}_6$ in orthopyroxene that were derived by Thompson (1970) in terms of atomic fractions of Mg and Fe in the M1 and M2 sites, the ideal version of which is the same as Saxena-Ghose-Mueller model.

Multicomponent-multisite extensions of the reciprocal solution model have been derived by Wood and Nicholls (1978), Sundman and Ågren (1981) and Hillert (1998) (the Swedish group was apparently unaware of the earlier work of Wood and Nicholls). In the metallurgical literature to which the last two studies belong, the model of activity expressions in terms of compositions of the different



lattice sites, such as in the equation (2.9), but involving additional activity coefficient terms resulting from the cross or reciprocal interactions between the sites, is known as the *sub-lattice model*. However, the credit for introducing the concept of relating the activity of a macroscopic end member to the compositions of lattice sites arguably belongs to Mueller (1962).

2.3.3 Inter-crystalline exchange equilibrium in non-ideal systems

Cation exchange thermometers have been usually formulated by retrieving the equilibrium constant of an exchange reaction of interest from experimental data for K_D at different temperatures and compositions in a binary system on the basis of equation (2.5). The pressure dependence of K_D is calculated according to $\partial \ln K_D / \partial P \approx \partial \ln K / \partial P = -\Delta V^\circ / RT$. This procedure implies that the partial molar volume change of a reaction is approximately the same as its molar volume change. The resulting error, if any, seems to be of little practical consequence, at least in most cases. Calibration of K as a function of temperature ($\ln K = -\Delta H^\circ / RT + \Delta S^\circ / R$) using the available thermochemical data is likely to be problematic because the exchange reactions have quite small enthalpy and entropy changes and their values in the databases may not be sufficiently accurate to yield well constrained relations between $\ln K$ and $1/T$ for the purpose of geothermometry. The optimisation procedure in the databases emphasises compatibility of the retrieved thermodynamic properties with experimentally determined phase diagrams that ensures internal consistency of the Gibbs free energy values ($G = H - TS$) of the phases rather than each of their components.

After one obtains an expression of $\ln K$ vs. $1/T$ with reasonable accuracy, the next step is to find an explicit expression for the $\ln K\gamma$ term in the equation (2.5) in order to be able to express $\ln K_D$ as a function of T , P and X . In the initial phase, this effort was limited to binary systems. For multicomponent systems, which are of much greater interest for the purpose of geothermometry, the compositional dependence of $\ln K_D$ was formulated at an early stage by statistical analyses of the available data of $\ln K_D$ vs. mineral compositions in suites of natural assemblages belonging to the same metamorphic grade (e.g., Saxena, 1969). Deviating from this trend, Ganguly and Kennedy (1974) developed a thermodynamic expression of the compositional dependence of $\ln K_D(\text{Fe-Mg})$ for garnet and biotite in a four component system according to equation (2.5) and a regular solution model for garnet (but neglecting ternary interaction terms). Their expression is as follows.

$$\ln K_d = \ln K(P, T) + \ln \left(\frac{\gamma_{Fe}}{\gamma_{Mg}} \right)^{Bt} + \frac{w_{12}}{RT} (X_{Fe}^{Grt} - X_{Mg}^{Grt}) + \frac{W_{23} - W_{13}}{RT} (X_{Ca}^{Grt}) + \frac{W_{24} - W_{14}}{RT} (X_{Mn}^{Grt}) \quad (2.10)$$

where W_{ij} is a binary interaction term in garnet with 1 standing for Fe, 2 for Mg, 3 for Ca, 4 for Mn and K is the equilibrium constant of the exchange reaction $\text{Mg-Grt} + \text{Fe-Bt} = \text{Fe-Grt} + \text{Mg-Bt}$ (with one mole of the exchangeable species)



so that $K_D(\text{Fe-Mg}) = (\text{Fe/Mg})^{\text{Grt}}/(\text{Fe/Mg})^{\text{Bt}}$ and $\ln K_D = \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Grt}} - \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Bt}}$. The expression for the activity coefficient of a quaternary regular solution used in the derivation of equation (2.10) was developed by Ganguly (1973).

The last three terms in the right of the above equation collectively stand for $-\ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Grt}}$; a similar set of terms would appear for the expression of $\ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Bt}}$ with appropriate change of sign that should be obvious. However, assuming biotite to be an ideal solution, which is a reasonable first approximation (Mueller, 1972), Ganguly and Kennedy (1974) carried out step wise multivariate statistical regression of a selection of the available data of $\ln K_D(\text{Fe-Mg})$ for coexisting biotite and garnet in staurolite grade rocks against the parenthetical compositional terms in the right hand side of the above equation. This exercise, coupled with some limited experiments on the homogenisation of mechanical mixtures of synthetic pyrope and grossular at different temperatures plus crystal chemical considerations, led to important constraints on the thermodynamic mixing properties of quaternary aluminosilicate garnet solid solutions that have been widely used in the early phase of thermobarometric calibrations and the estimation of P-T conditions of metamorphic rocks. The above equation also initiated a thermodynamic route for the treatment of the compositional dependence of a distribution coefficient that has been adapted by others to develop geothermometric equations and retrieve thermodynamic mixing properties.

The Ganguly and Kennedy (1974) paper got a scathing review from an anonymous reviewer. Any other editor would have very likely rejected the paper, but Bill Fyfe, who was the executive editor of the *Contributions to Mineralogy and Petrology* and handled the paper himself, sent the review to me and asked if I would like to respond to the comments. It was likely that given his knowledge of thermodynamics, he did not think that the comments by the reviewer were correct. I was very upset – it was the first paper that I wrote after Kennedy gave me the “do whatever you want” liberty – and spent a few agonising days to write a point by point response to the reviewer’s comments. I then took the paper and my response to Kennedy. Skimming through the review and listening to what I had to say, Kennedy asked his secretary to make an appointment with Bob Scott in the UCLA Chemistry department and told me that he would have Bob Scott look at the paper and the reviewer’s comments. This was the famous authority of thermodynamics, Robert L. Scott, the inventor of the Regular Solution model (see above).

After a couple of weeks, I saw Kennedy walking towards his office with a smiling face and some papers rolled in his hand and as soon as he saw me, he told me that he was coming from Bob Scott’s office. He handed the rolled up papers to me, which happened to be the manuscript of our paper, and said that Bob was sorry that it took him so long (he was probably also the departmental head at that time) but he had gone through the paper carefully and found it to be quite interesting. And to avoid a potential struggle down the road, Bob Scott wrote the response to the reviewer’s comments himself (it was an old fashioned writing in pencil on yellow pages of a tablet), and also made some minor suggestions that I should take care of in the revision. Kennedy sent the typed copy of Bob Scott’s



response to Bill Fyfe along with the revised version of the manuscript and after about a week, he received a brief letter from Fyfe saying that the manuscript was “on its way to the press”. I have been told by Bob Newton that Kennedy sometimes referred to me as “gold plated Ganguly”, and I think this flattering transition from Bob Berner’s “my first guinea pig” (Section 1.4.1) took place with the Ganguly and Kennedy (1974) paper. It seems likely that the emergence of the field of thermobarometry of metamorphic rocks might have been significantly delayed if the paper by Ganguly and Kennedy (1974) had been rejected (*e.g.*, see Section 5.2; Ghent, 1976).

In a small and focused international conference in the Pennsylvania State University in 1975 (more on this conference in Section 3.3), Bob Newton pulled me aside one evening and unfolded a hand drawn graph to show the heat of solution data in the pyrope-grossular join as a function of composition (later published as Newton *et al.*, 1977) (this was a part of the long Newton-Kleppa collaboration discussed in the Section 1.3). The data were in very good agreement with the excess enthalpy of mixing predicted by the Ganguly-Kennedy model of garnet solution property within the compositional range (metapelitic garnets) encompassed by the model. This success at a very early stage of my professional career was a significant confidence booster for me!

Now returning to the main theme in this section, the expression of $\ln K_D(i-j)$ for exchange reactions that involve mineral(s) with multi-site substitution, the activity coefficients need to be expressed in terms of the reciprocal solution model. As an example of this approach, let us consider the Fe^{2+} -Mg exchange equilibrium between spinel (Sp: $(Fe^{2+}, Mg)(Al, Cr)_2O_4$) and olivine (Ol: $(Fe^{2+}, Mg)_2SiO_4$):



for which $K_D = (Fe^{2+}/Mg)^{Sp}/(Fe^{2+}/Mg)^{Ol}$. If mixing of the cations in their individual sites is ideal, then using the reciprocal solution model for the activity coefficients of $FeAl_2O_4$ and $MgAl_2O_4$ in spinel, it can be shown that

$$\ln K_D(Fe^{2+} - Mg) = \ln K_{(d)} + \frac{\Delta G_{(e.rec)}^o}{RT} Y_{Cr} \quad (2.11)$$

where $Y_{Cr} = Cr/(Cr + Al + Fe^{3+})$ in the octahedral site of spinel, $K_{(d)}$ is the equilibrium constant of the Fe^{2+} -Mg exchange reaction (2.d), and $\Delta G_{(e.rec)}^o$ is the standard state free energy change of the reciprocal reaction



Figure 2.5a, which is reproduced from Evans and Frost (1975), illustrates the dependence of $\ln K_D(Fe^{2+}-Mg)$ in Sp-Ol pairs Y_{Cr}^{Sp} on in a suite of chlorite-enstatite-olivine-spinel rocks with a dilute and nearly constant mole fraction of Fe^{3+} ($X_{Fe^{3+}}$) in the octahedral or Al-site of spinel. The observed relation conforms to the form of equation (2.11). A similar linear relation between $\ln K_D(Fe^{2+} -Mg)$ and Y_{Cr} was found by Liermann and Ganguly (2003) in their experimental study of Fe^{2+} - Mg fractionation between spinel and orthopyroxene as a function of temperature and composition (Fig. 2.5b).



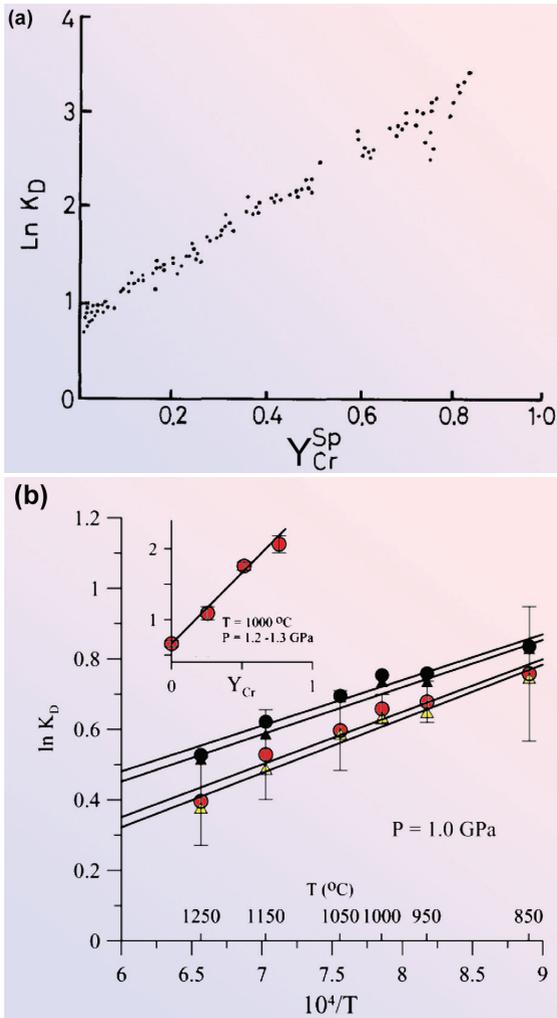


Figure 2.5

Effect of (a) Cr content in the octahedral site of spinel on the $\ln K_D(\text{Fe-Mg})$ between spinel and olivine in a suite of spinel-olivine-enstatite-chlorite rocks (Evans and Frost, 1975) and (b) effects of Cr in spinel (inset) and temperature on $\ln K_D(\text{Fe-Mg})$ between spinel and orthopyroxene, as determined experimentally by Liermann and Ganguly (2003). $Y_{Cr} = \text{Cr}/(\text{Cr}+\text{Al}+\text{Fe}^{3+})$; the Fe^{3+} is nearly constant in the octahedral site of spinel with a mole fraction of ~ 0.05 in (a) and ~ 0 in (b: inset). Black and coloured symbols in the main figure: with and without correction for the effect of Al in Opx on the K_D values, respectively; triangles and circles represent two different schemes of estimation of Fe^{3+} in spinels. Modified from Liermann and Ganguly (2003).



Liermann and Ganguly (2003) also presented the $\ln K_D(\text{Fe}^{2+}\text{-Mg})$ vs. Y_{Cr} relation at 600-1300 °C by retrieving $\Delta G_{(e.rec)}^0$ from the experimental data illustrated in the Figure 2.5b (inset), according to equation (2.11), and assuming, following a suggestion by F orland (1964), that the standard state entropy change of a reciprocal reaction is negligible (this makes $\Delta G_{(e.rec)}^0$ independent of temperature). Their results are in very good agreement with the those of the more elaborate treatment of the problem by Sack and Ghiorso (1991) within the temperature range 700-1300 °C and up to $Y_{\text{Cr}} \sim 0.3$ at 600 °C; the results of Liermann and Ganguly are also in excellent agreement with the natural data illustrated in Figure 2.5a for which the temperature was estimated to be 700 °C. Sack and Ghiorso (1991) also discussed the effect of Cr/Fe³⁺ ratio on $\ln K_D(\text{Fe-Mg})$ between olivine and spinel. The best approach to olivine-spinel Fe-Mg exchange thermometry may be to combine the calibration of Liermann and Ganguly (2003) between olivine and aluminous spinel, (Fe,Mg)Al₂O₄, and the effect of Cr and Fe³⁺ in the octahedral site of spinel from Sack and Ghiorso (1991).

2.3.4 Trace element and single mineral thermometry/barometry

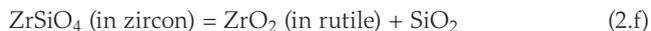
I have not been involved in any work in these fields that are becoming quite popular in the field of petrology. However, I take this opportunity to comment on the thermodynamic basis and historical context of these classes of thermometers and barometers.

The thermodynamic basis of trace element thermometry rests on the Henry's law behaviour, or assumption of that behaviour, of the trace components used in specific thermometric formulations. When a trace element thermometer is formulated in terms of the ratio of mole fraction or weight percent of a very dilute component in two phases, it is based on the Nernst distribution law (equation (2.2)) that has been derived above as a limiting case of inter-crystalline ion exchange equilibrium and assuming Henry's law behaviour of the trace component in both phases. However, as emphasised above, the value of the constant, K' depends on the solvent composition. Thus, a trace element thermometer calibrated as a function of temperature for one set of compositions of the two phases may not necessarily hold for a different set, unless both solid phases behave as ideal solutions.

As discussed in Section 2.2.1, Kretz (1959) may be regarded as the one laying the observational foundation of the field of trace element thermobarometry by showing that the trace element content of one mineral varies as a constant proportion of that in a coexisting mineral, as predicted by equation (2.2) (Fig. 2.1c), at least in high T metamorphic rocks. Several trace element thermometers have now been calibrated experimentally or empirically for applications to petrological problems (e.g., Ferry and Watson, 2007; Liang *et al.*, 2013; Pickles *et al.*, 2016). An insightful review of the field may be found in Essene (2009).



A trace element thermometer such as “Zr-in-rutile” focuses on the dependence of the content of one element in a phase on temperature at a fixed pressure. However, the content of the chosen element in a phase may depend on the activities of other components and care must be taken to correct for the difference of the “other activities” between the calibration experiments and natural assemblages. To explain this point, let us consider the specific case of “Zr-in-rutile” thermometer that was calibrated by Ferry and Watson (2007) and for which the governing equilibrium is as follows.



The equilibrium constant for this reaction, $K_{(f)}$, is given by

$$\ln K_{(f)} = -\frac{\Delta G_f^{\circ}(P, T)}{RT} = \ln a_{\text{ZrO}_2}^{\text{rutile}} + \ln a_{\text{SiO}_2} - \ln a_{\text{ZrSiO}_4}^{\text{zircon}} \quad (2.12)$$

Regardless of their individual values, the sum of the terms after the second equality defines the equilibrium constant that is a function of only P and T. Ferry and Watson (2007) assumed that the activity coefficient of ZrO_2 in rutile obeys the Henry’s law behaviour (*i.e.* $a_{\text{ZrO}_2}^{\text{rutile}} \propto X_{\text{ZrO}_2}^{\text{rutile}}$) so that $a_{\text{ZrO}_2}^{\text{rutile}} = k(\text{ppm Zr}^{\text{rutile}})$, where k is a constant that is a product of Henry’s law constant and the factor that relates ppm Zr to the mole fraction of ZrO_2 in rutile. Based on their experimental data at 10 kb and data from natural samples, Ferry and Watson (2007) calibrated $\log(\text{ppm Zr}^{\text{rutile}})$ as a function of T at unit activities of SiO_2 and ZrSiO_4 defined, respectively, by the presence of α -quartz and pure zircon. This calibration yields an expression of $\ln K_{(f)}$ as a function of T (since at unit activities of SiO_2 and of ZrSiO_4 in zircon, $\ln(a_{\text{ZrO}_2}^{\text{rutile}})$ vs. T is the same as $\ln K_{(f)}$ vs. T), leading finally to the following thermometric equation.

$$\log\left(\text{ppm Zr}^{\text{rutile}} \text{ at } a_{\text{ZrSiO}_4}^{\text{zircon}} = 1\right) = 7.42(\pm 0.105) - \frac{4530(\pm 111)}{T(K)} - \log a_{\text{SiO}_2} \quad (2.13)$$

Correction for the effect of pressure may be done according to $\partial \ln(\text{ppm Zr}^{\text{rutile}})/\partial P \sim \partial \ln K/\partial P = -\Delta V^{\circ}/RT$.

Ferry and Watson (2007) noted that zircon may deviate from a $\text{Zr}(\text{Si,Ti})\text{O}_4$ solid solution by incorporation of other elements such as Hf, U and Th. In that case following the equation (2.12), a $\log a_{\text{ZrSiO}_4}^{\text{zircon}}$ term may have to be added to the right hand side of the above equation depending on whether or not $X_{\text{ZrSiO}_4}^{\text{zircon}}$ significantly deviates from unity. An additional problem may arise regarding the value of Henry’s law constant that is incorporated in the constant term in the above equation. As discussed by Lewis and Randall (1961, Chapter 34), even at very low concentrations, there may be significant interactions between dilute components.

According to Duhem’s theorem (see, for example, Ganguly, 2020), there are only two independent variables for a closed system (*i.e.* a system of fixed bulk composition). These variables may be extensive or intensive or a combination



of both (the number of intensive variables that may be specified is, of course, restricted by the Phase Rule). Thus, of the three variables in a closed system, namely P, T and the composition of a phase, there are only two independent variables. And there lies the thermodynamic basis of a single mineral thermometry or barometry that consists of a relationship among P, T and a single mineral composition that is sensitive to change of T and/or P (e.g., Nimis and Taylor, 2000). Thus, care must be taken to ensure that the natural sample to which a single mineral thermometric or barometric calibration is applied has effectively the same bulk composition as that used in developing the calibration. Some experimental tests should also be undertaken to evaluate the sensitivity of the mineral composition of choice to changes of bulk composition within the range encompassed by the natural assemblages.

2.4 Kinetics of Exchange Reactions: Transition to Geospeedometry

In their classic study of palaeotemperature based on $^{18}\text{O}/^{16}\text{O}$ fractionation between the ocean water and a Jurassic belemnite from the Isle of Skye, Scotland that has been discussed in the Section 1, Urey *et al.* (1951) were the first to deal with the issue of possible diffusive resetting of a thermometer over geological time scale. However, the impetus for studying the kinetic response of intra-crystalline and oxygen isotopic exchange thermometers came from the recognition that the temperatures calculated for many slowly cooled samples from metamorphic and igneous rocks are much lower than what one would infer from their primary mineralogical characteristics (e.g., Bottinga and Javoy, 1975; Ganguly, 1982a). Furthermore, when the compositions within mineral grains with micron scale resolution became measurable with the introduction of microprobe in the mid- 1960s, it was found that many minerals in slowly cooled rocks are compositionally zoned. And in many cases the reason seemed to be the change of compositions at the mineral-mineral interfaces, where equilibrium was achieved more quickly than in the interior of a grain in response to change of K_D during cooling. These observations of resetting of mineral compositions gave birth to the field of geospeedometry, a term coined by Lasaga (1983). It may be emphasised at the outset that a single method only constrains the T-t path or cooling rate around the temperature of quenching of the specific mineralogical property (ordering state, compositional zoning, mineral age determined by a particular decay system) that is being modelled, and not through its entire cooling regime.

2.4.1 Intra-crystalline exchange or order-disorder

Since the pioneering studies by Virgo and Hafner (1969, 1971), Saxena and Ghose (1971) and Hafner and Ghose (1971), thermometers based on Fe-Mg exchange between non-equivalent octahedral sites in pyroxenes and amphiboles have been experimentally calibrated by several workers using single crystal structure refinement or Mössbauer spectroscopy as the primary analytical tools (e.g., Besancon,



1981; Annovitz *et al.*, 1988; Skogby, 1992; Zema *et al.*, 1997; Heinemann *et al.*, 2000; Wang *et al.* 2005). A comprehensive discussion of these and other methods for the determination of the site occupancies may be found in Ghose (1982).

Mueller (1967b, 1969b) formulated the kinetic theory of intra-crystalline exchange between two non-equivalent sites of a mineral using a chemical rate theory approach that was first introduced by Dienes (1955) to deal with metallic solid solutions¹⁴. This formulation enables calculation of the change of ordering state of a mineral as a function of time under isothermal condition, and requires knowledge of the rate constant, bulk composition, multiplicities of the sites and the intra-crystalline (equilibrium) distribution coefficient, k_D (here I am using lower case k to distinguish the distribution coefficient from the inter-crystalline distribution coefficient, K_D). Mueller's theory was extended by Sha and Chappell (1996) for two site multicomponent systems. A Landau theory based approach to the cation ordering kinetics was presented by Salje and Kroll (1991). As discussed by them, the chemical rate theory of Mueller (1967b, 1969c) follows as a special case of the Landau theory and has the advantage of physical appeal. All experimental data on Fe-Mg order-disorder in quasi-binary systems have been found to conform to Mueller's chemical rate theory.

One of the very early studies of cooling rate of rocks was by Seifert and Virgo (1975), who applied Mueller's kinetic theory to estimate the time needed to achieve the observed Fe-Mg ordering state of an anthophyllite (approximated as a two site crystal: M1+M2+M3 and M4) in a rock sample from the Precambrian Dillion complex, Montana; the site occupancies were determined by Mössbauer spectroscopy. However, they used a metallurgical approach in which the time needed to quench an ordering state through continuous cooling is equated to that under isothermal condition at the quenching temperature. Recognising that this approach underestimates cooling rate, Ganguly (1982a) developed a numerical approach in which the change of ordering state as a function of time during cooling is calculated through a series of small isothermal steps according to Mueller's rate equation. This method has been applied to constrain thermal histories of many asteroidal (*e.g.*, Ganguly *et al.*, 1994, 2013; Zema *et al.*, 1997), terrestrial (*e.g.*, Ganguly and Domeneghetti, 1996; Stimpfl *et al.*, 2005) and lunar samples (McCallum *et al.*, 2006).

14. Mueller (1962) recognised a distinction between the disordering processes in metallic alloys and mineral solid solutions in terms of the extent of feedback between the disordering energy and the extent of disordering; greater the disorder, lower is the energy requirement to disorder as the non-equivalent lattice sites become progressively similar. In metallic alloys (*e.g.*, FeNi), the cooperative effect is strong since all lattice sites are involved in the order-disorder process so that beyond a critical temperature an alloy disorders very rapidly to a completely disordered state. In a mineral (*e.g.*, pyroxene), on the other hand, only a small fraction of the total lattice sites participates in the order-disorder process and the geometries of these sites are determined primarily by the non-participating rigid framework. Following the nomenclature of Thompson (1969), the two types of disordering in the alloy and mineralogical systems are commonly referred to, respectively, as convergent and non-convergent disordering in the mineralogical literature.



Figure 2.6a shows an example of the simulated evolutions (Stimpfl *et al.*, 2005), according to the method of Ganguly (1982a), of the M2 site occupancy of Fe in several orthopyroxene crystals from the Khtada Lake metamorphic complex, British Columbia. The cooling was assumed to follow an asymptotic form, *viz.* $1/T(K) = 1/T_o + \eta t$ where T_o is the initial temperature from which the system cooled and η is a cooling time constant (with dimension of $K^{-1}t^{-1}$) so that $dT/dt = -\eta T^2$. The η value shown in the diagram led to quenched X_{Fe}^{M2} values matching the measured ones for different crystals. The measured site occupancies are illustrated by symbols with $\pm 2\sigma$ error bars; the difference among the X_{Fe}^{M2} values of different crystals stems from that of their bulk Fe/(Fe + Mg) ratio. The η value was varied in the simulations until the observed site occupancies of all crystals were simultaneously reproduced within the errors of their measurements. This type of simulation is insensitive to the assumed value of T_o (which was set at 400 °C in this study) as long as it is ~50 °C above the onset of the deviation of the simulated path from the corresponding equilibrium path (dashed lines in the figure). Thermometric calibration of $k_D(Fe-Mg)$ yielded a narrow range of 283-294 °C (average 288 °C) as the closure temperature, T_c , of the observed ordering states. These temperatures are well reproduced by the projection of the quenched limbs of the simulations on to the corresponding equilibrium paths. Figure 2.6b shows a comparison of the retrieved cooling rates near the quenching temperatures with the T-t path constrained by the conventional age-closure temperature combination of multiple geochronological systems.

Figure 2.6a illustrates a general point about the meaning of the temperature calculated from an observed compositional property of a system. It is not the quenching temperature, T_q , of the observed property but is a temperature, T_c ($>T_q$), at which the system would have attained the observed property if it had maintained equilibrium with the changing thermal condition during cooling. The difference between T_c and T_q depends on the cooling rate and activation energy of the specific rate process (Ganguly, 1982a).

The cooling rate calculations of natural samples are very sensitive to errors in the determination of site occupancies, especially at low concentrations of Fe (Ganguly *et al.*, 1989). Also, it seems that site occupancies of samples determined by Mössbauer spectroscopy and single crystal X-ray diffraction differ even after most careful spectroscopic and structure refinement protocols (Wang *et al.*, 2005). Thus, it is better not to mix the two protocols for the experimental calibration of the dependence of k_D on T and the determination of site occupancies of natural samples. My preferred calibration using the structure refinement method is the one by Stimpfl *et al.* (1999) and that using Mössbauer spectroscopy by Wang *et al.* (2005). The rate constants determined according to the methods are, however, quite similar. This implies that both methods suffer from intrinsic errors that cancelled out when one determined the time dependency of the site occupancy to derive the rate constants.



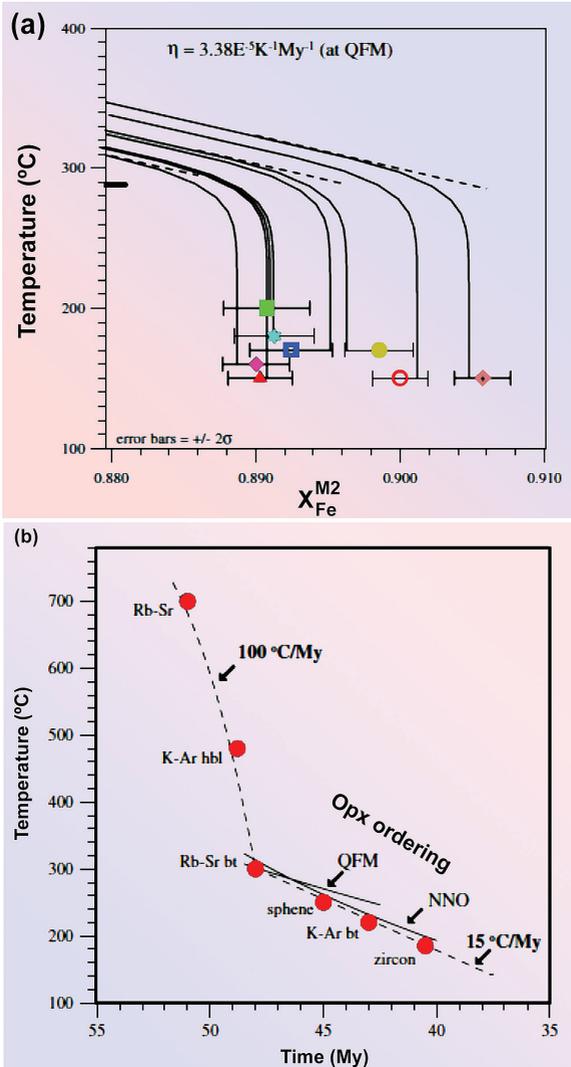


Figure 2.6

(a) Simulated evolution of Fe-Mg ordering states, denoted as X_{Fe}^{M2} (Fe/(Fe+Mg) in the M2 site) of orthopyroxene crystals from the Central Gneissic Complex, British Columbia. The symbols are the observed site occupancies ($\pm 2\sigma$) of the crystals with different Fe/(Fe+Mg) ratios; the temperature axis has no relevance for these data. (b) Comparison of T-t path constrained by geochronological data with those deduced from the Fe-Mg ordering states of orthopyroxene crystals using rate constants determined at $f(O_2)$ of QFM (quartz-fayalite-magnetite) and NNO (Ni-NiO) buffers. Modified from Stimpfli *et al.* (2005).



My work on the Fe-Mg order-disorder in minerals had been primarily funded by NASA. But my first proposal to NASA in the early 1990s to study the Fe-Mg ordering states of meteoritic orthopyroxenes and carry out the necessary kinetic experiments to retrieve the cooling rates of meteorites was unsuccessful. I mentioned this to my colleague and good friend, Mike Drake, by then a very prominent figure in the NASA circle, and Mike told me to have a meeting with him in a pub known as Gentle Ben, just outside the boundary wall of the campus. By the time I arrived – I was about 5-10 minutes late – Mike was already down to almost half the pitcher, all by himself (people who knew Mike would have no problem believing this). As we settled down for lunch, Mike explained to me that NASA had a different funding outlook than NSF (National Science Foundation) in that once someone was on board, NASA would like to keep that person on board for some time provided, of course, that he/she was able to come up with interesting ideas in each funding cycle and had shown satisfactory progress in the previous cycle. Thus, NASA wanted to be satisfied that the investigator had a long- term commitment for research activities within the scope of its funding opportunities and was not a transient who was trying to get some interim funding to sail through a dry period with NSF. Since very few people in the NASA circle had even seen my face, the first thing for me to do, Mike suggested, was to present a paper at the LPSC (Lunar and Planetary Science Conference) at Houston.

I followed Mike's advice. My talk was scheduled to be the last one (or very close to the end) of the morning session, but Mike made sure that the important figures did not leave before my talk. He forewarned me that it better be "the best talk of your life". After the session ended, Gerry Wasserburg walked up to me – he did not know me before – and said: *Very interesting stuff; are you going to pursue it?* After thanking him for his compliments, I mentioned to him that I had published a major paper on the general theory with applications to terrestrial problems and would like to expand the scope to planetary problems if I succeeded in getting support from NASA. Wasserburg asked me to send him my paper, which I, of course, did, but I also took this opportunity to send him a copy of my rejected NASA proposal. Encouraged by the reaction of Wasserburg and the positive comments of some others in the audience that included my professor from Chicago, Bob Clayton, I resubmitted my proposal with some revision and finally got funded. And thus began my almost 25 years of continued funding from NASA and research programmes in planetary sciences. Of course, with time I branched out in different directions of planetary research.

Text Box 2.5 – My impression of Gerry Wasserburg

This NASA meeting was my only face to face interaction with Wasserburg, but I heard from others that he had little tolerance for what he thought as nonsense (I saw that in meeting situations). Many years later, the Mg-Fe diffusion kinetic data for spinel by one of my students, Peter Liermann, turned out to be in disagreement with those in a paper coauthored by Wasserburg (Sheng *et al.*, 1992). I wrote an e-mail to him discussing the problem, offering an explanation about the disagreement and asking if he could arrange to send me one of the spinel samples used in their experiments



so we can do a careful microprobe analysis of the samples. I got a quick reply from Wasserburg saying that the explanation that I offered seemed quite reasonable (see Liermann and Ganguly, 2002); however, the student that worked on this problem had left and it would require quite a bit of searching by him in his lab to find out if the samples were still there. However, he added that if I still felt a need to look at the samples, he would try to find them. It seemed to me that even though he was an extremely busy person and might have had little tolerance for nonsense, Wasserburg was probably never too busy to spend his time to resolve a sensible scientific issue, even if the outcome had the chance of going against his own work.



Figure 2.7 Alberto Dal Negro (right) presenting what looks like a very attractive gift to Volkmar Tromsdorff (1936-2005) after his talk at the Annual Meeting of the Italian Mineralogical Association in Padova in 1991.

My research on the thermodynamics and kinetics of Fe-Mg order-disorder in orthopyroxene and their applications to determine the cooling rates of meteoritic and terrestrial samples flourished through collaboration with Subrata Ghose and his student, Hexiong Yang, and the Italian group of crystallographers, Chiara Domeneghetti, Victorio Tazzoli and Gianmario Molin. In 1991, I was invited to give a planetary talk in the annual meeting of the Italian Mineralogical Society in Padova and there I found that my 1982 paper on the thermodynamics and kinetics of Fe-Mg order-disorder in minerals had caught a lot of attention among the Italian group. The head of Mineralogy and Petrology of the University of Padova, Alberto Dal Negro (Fig. 2.7), and the others invited me for a follow up visit to Italy



that I gladly accepted. Who would not, considering the warmth of the people, the history and culture, beauty of the land and may be, above all, the attraction of the food and wine? The next year I took advantage of my sabbatical leave and visited the University of Padova and Pavia to begin what turned out to be a long period of collaborative research not only with the Italian crystallographers, but also with the outstanding Italian geochemist, Giulio Ottonello (Fig. 2.2). I first met Giulio earlier in a GSA meeting in USA, but that initial acquaintance became a deep friendship between our families through many subsequent visits both ways across the Atlantic. Also, two Italian students, Marilena Stimpfl and Max Tirone, came over to work with me for their Ph.D. degrees, with Marilena's principal focus of research being the thermodynamics and kinetics of Fe-Mg order-disorder in orthopyroxene (see Fig. 2.6).

2.4.2 Inter-crystalline exchange

With the introduction of electron microprobe into petrological research, it became evident that many minerals such as garnet, pyroxene *etc.* show systematic compositional variations from core to rim within individual grains in slowly cooled rocks. Some of these zonings are attributable to the change of equilibrium fractionation between coexisting minerals at their interface and the sluggishness of the crystal interiors to equilibrate with the interface composition during cooling, thus leading to the development of a (retrograde) zoning profile near the grain boundary. In two pioneering contributions, Lasaga and co-workers (Lasaga *et al.*, 1977; Lasaga, 1983) showed how these retrograde profiles may be modelled to extend geothermometry to geospeedometry and presented mathematical treatment of the development of diffusion induced compositional profiles within coexisting minerals as function of cooling rate (see also the work of John Wood (1964, 1965) and Goldstein and Ogilvie (1964) on metallographic cooling rates of meteorites in Section 1). Lasaga (1983) derived an analytical solution for the development of zoning profiles in two coexisting minerals, subject to the flux balance condition (*i.e.* the mass of a component gained by a mineral is exactly the same as that lost by the adjacent mineral) and assuming that the effect of diffusion during cooling did not affect the core compositions of the crystals (Fig. 2.8). The cooling rate was assumed to have remained constant and certain simplifying assumptions were also made about the change of interface composition during cooling to make the problem accessible to analytical solution. These studies were followed up by many workers to model retrograde zoning in minerals to constrain cooling rates of rocks and also prompted experimental and theoretical studies to determine the diffusion kinetic properties of minerals that exhibit retrograde zoning in metamorphic, igneous and meteorite samples.



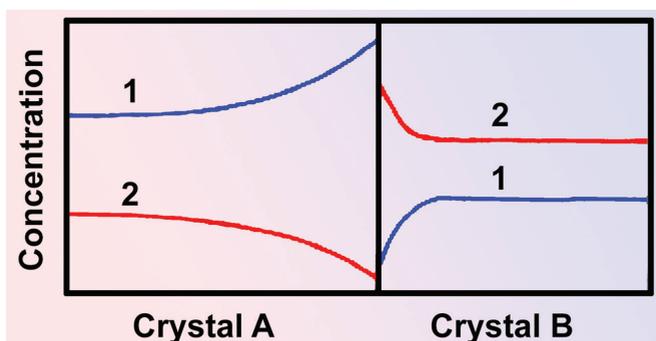


Figure 2.8 Schematic illustration of the development of compositional profiles in two adjacent minerals, which were initially homogeneous, in response to changing interface compositions satisfying the K_D vs. T relation during cooling until the diffusion becomes too slow to have any measurable effect on the compositional profiles. Modified from Lasaga (1983).

The analytical solution of Lasaga (1983) for the calculation of a quenched profile in a mineral involves a summation series from zero to infinity that converges rather slowly (Ganguly *et al.*, 2000). With the wide availability of high speed desk/lap-top computers, it was found to be more efficient to calculate the profiles using an efficient numerical method (*e.g.*, the Crank-Nicolson implicit scheme) that also gives greater flexibility on the forms of the T - t relation and the change of interface composition. An example of such modelling of compositional profiles (Ganguly *et al.*, 2000) is illustrated in Figure 2.9, which shows the variation of Mg# (*i.e.* Mg/(Mg + Fe) molar ratio) near the rim of a garnet sample adjacent to a relatively large mass of biotite; the model fits to the data along two microprobe line scans are illustrated by solid lines. The modelling assumes that (a) the biotite behaved as a homogeneous semi-infinite reservoir so that there was effectively no change of its composition, and (b) the garnet behaved as a semi-infinite medium so that its core composition was unaffected by diffusion. The sample was from the High Himalayan Crystalline (HHC) schist in Sikkim, near the South Tibetan Detachment System. Geothermometry based on Fe-Mg fractionation between garnet and biotite yielded ~450 and 800 °C using, respectively, the rim and core composition of the garnet. The composition of adjacent and distant biotite was found to be the same, thus constituting the justification for the assumption (a). The assumption (b) was justified by the fact that the core of composition of the zoned garnet was the same (within analytical error) as that of unzoned garnets within a quartzofeldspathic matrix that effectively insulated the transport of material in/out of the garnet grains. The reconstruction of the P - T path of this sample by coupling the diffusion kinetic modelling with heat transfer relation is discussed further in Section 5.1.



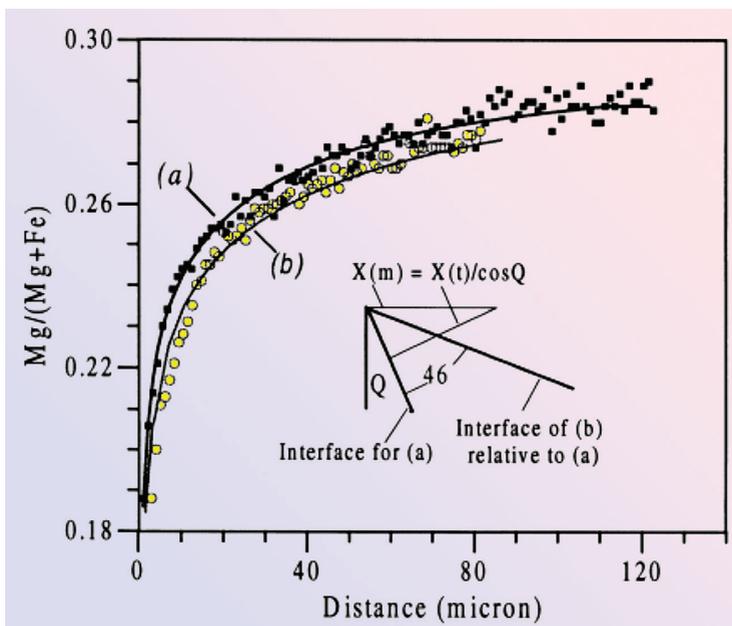


Figure 2.9

Observed variation of Mg# in a garnet crystal (symbols) adjacent to a large mass of biotite along two transects normal to the interface between the minerals in the plane of the thin section. The curve (a) is a model fit to the filled squares according to numerical solution of the diffusion equation (see text); the curve (b) was derived from (a) by 46° counter-clockwise rotation of the interface (inset) and fits the data along another traverse (circles) very well. $X(m)$: the measured profile length when the orientation of the interface deviates by an angle Q from the vertical; $X(t)$: length of the diffusion profile normal to the interface. Modified from Ganguly *et al.* (2000).

It is now interesting to consider the limiting case of an “ideal” geothermometer that did not suffer from any measurable diffusive readjustment of compositions of adjacent minerals within the time scale of cooling of the rock. This type of data was modelled by Ganguly *et al.* (2013, 2016) for co-existing enstatite and diopside in chondritic meteorites in which the Fe-Mg compositional profiles were measured in an electron microprobe at 1 mm step using a finely focused beam. Two examples of such data and modelling are illustrated in Figure 2.10. The modelling of the “flat” profiles allowed for the convolution effects due to the spatial averaging in microprobe analyses near the interface of a mineral pair, according to the method of Ganguly *et al.* (1988).



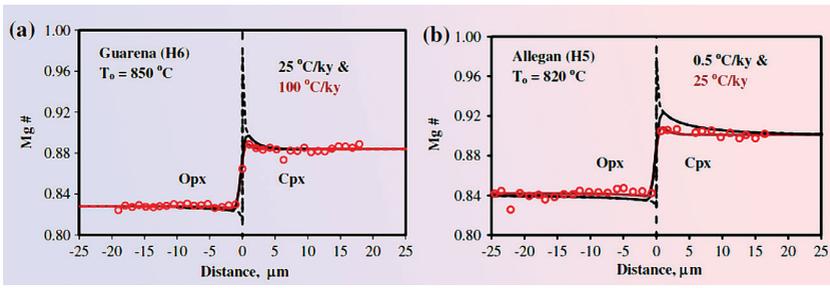


Figure 2.10 Modeling of flat compositional profiles in orthopyroxene-clinopyroxene (Opx-Cpx) pairs in two chondritic meteorite samples to retrieve their limiting cooling rates. The red circles represent microprobe data for Mg# ($Mg/(Mg+Fe)$) in the samples belonging to the composition-metamorphic grades H6 and H5 (H: high iron; number: metamorphic grade, increasing with number). The dashed lines are simulated profiles with the indicated cooling rates, and the solid lines are the corresponding profiles after correction for the convolution effect near the interface. Modified from Ganguly *et al.* (2013).

It was found that the slow cooling rates (\sim degrees/Myr), which were constrained at temperatures below ~ 500 °C for several samples by other types of data (thermochronological, metallographic and cation ordering of orthopyroxene), are incompatible with the observed flat compositional profiles for the samples. Preservation of such compositional profiles requires very rapid cooling on the order of degrees/kyr. An example of the retrieved cooling rates at both high and low temperature regimes for a specific chondrite sample, St. Séverin, is shown in Figure 2.11. This type of dramatic difference in the cooling rates between high and low temperature regimes for several samples of chondrites of different chemical and metamorphic types, as well as from stony-iron meteorites known as mesosiderites (Ganguly *et al.*, 1994), suggest impact induced breakup of the parent bodies of the meteorites in the early history of the solar system (4555-4560 Myr before present) and their subsequent reassembly under a regolith blanket on the same or different asteroidal bodies permitting slow cooling (Ganguly *et al.*, 2013, 2016). A number of later studies have indeed presented evidence for impact induced breakup of the asteroidal parent bodies.



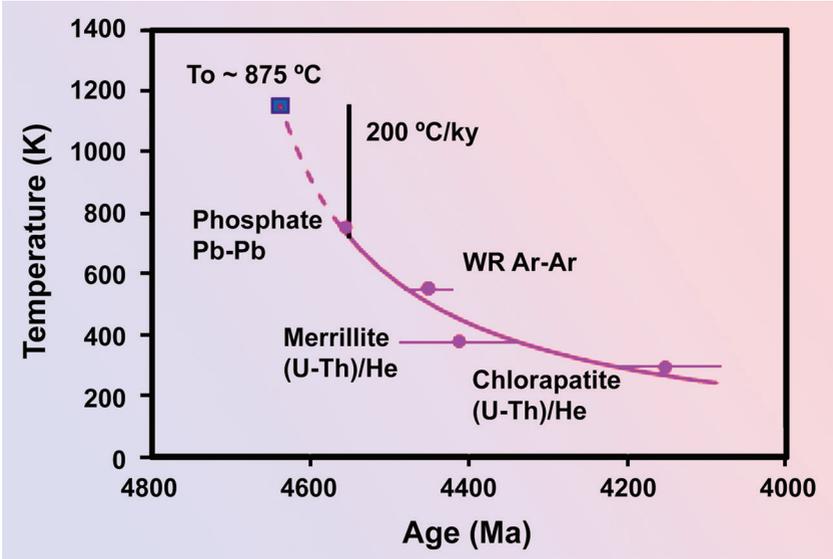


Figure 2.11

Thermochronological data (T_c vs. age: filled circles with the quoted error bars from the original sources) for the chondrite sample, St. Séverin, which were fitted by an asymptotic cooling model, $1/T(K) = 1/T_0(K) + \eta t$, with $h = 6(10^{-6})/K\text{-My}$, and extrapolated to the peak temperature, 875 °C, as determined from $K_D(\text{Fe-Mg})$ between adjacent and homogeneous grains of ortho- and clino-pyroxenes. The vertical line shows the high-temperature segment of the cooling history retrieved from modeling flat compositional profiles of co-existing pyroxene crystals. Modified from Ganguly *et al.* (2016).



3.1 Experimental Calibrations: Methodology and Thermodynamic Basis

Experimental calibration of a mineral reaction is expected to tightly constrain its equilibrium condition as a function of the intensive variables of interest in a specific study. The most unambiguous way of achieving this objective is to determine “reversal brackets” using crystalline starting mixtures of both the reactant and product phases. For an end member reaction, a reversal bracket consists of a pair of closely spaced P-T points at which the product grew at the expense of the reactant and *vice versa*. The relative proportion of the product and reactant phases are commonly determined by comparing the powder X-ray diffraction pattern of the mixture before and after an experiment, taking care to eliminate the effect of preferred orientation of platy minerals on the peak height intensities. The method of using reversal brackets for the determination of equilibrium reaction boundaries of stoichiometric phases was introduced by Newton and Kennedy (1963) in connection with their investigation of the stability of lawsonite and zoisite. I learned this technique from Newton during the course of my Ph.D. research and passed it on to my students and others.

The basic thermodynamic idea behind the technique of “reversal brackets” is that if a phase or an assemblage of phases transforms to a different one, then the latter must have lower free energy than the other at the experimental condition. Thus, for a reaction of say $A + B = C + D$ a “reversal bracket” defines a narrow space in which the free energy of $C + D$ is lower than that of $A + B$ at one end of the bracket while the reverse situation holds at the other end. The experiments are carried out by subjecting a finely ground mixture of the reactant and product phases, commonly with water as a catalyst even if the reaction itself is a completely solid state reaction, to desired P-T conditions. Intense grinding may, however, introduce a surface free energy effect, as was demonstrated by Newton (1969) in his investigation of the kyanite-sillimanite equilibrium, making a phase or an assemblage unstable at a P-T condition that is within its “normal” field of stability when the surface free energy effect is negligible. (The surface free energy effect becomes important at submicron grain size, especially below 0.1 micron; see Ganguly, 2020, Sections 13.10 and 13.13)

A set of reversal brackets constrains the location of a line in the P-T space (or in that of any other chosen pair of independent intensive variables) at which the Gibbs free energies of the two isochemical assemblages are equal. In a synthesis experiment, the assemblage of phases that tend to form within short duration experiments is the one that has the smallest activation energy barrier in the kinetic pathway and does not necessarily correspond to that defining the lowest free energy state relative to the other isochemical assemblages. A familiar example is the metastable vapour phase synthesis of diamond. Many examples



of formation of metastable phases in synthesis experiments may be found in the literature of experimental petrology in its early period. The wide scatter in the experimental determination of the aluminum silicate triple point (Fig. 3.4) and the phase relations of peridotite in the MAS system using both synthesis and “reversal bracket” procedures (Fig. 3.3a,b, respectively), which are discussed in the following section, highlight the problem that one may face by relying on the results of syntheses or unreversed experiments. The syntheses experiments have value in providing a quick overview of what may be expected at certain conditions, but they should be followed up by reversal experiments to establish the equilibrium situations.

Text Box 3.1 – Friction correction in piston-cylinder experiments

To determine the equilibrium P-T trajectory of a pressure sensitive reaction in the piston-cylinder apparatus that is to be used for the purpose of geobarometry, it is also important to use a proper friction correction that accounts for the difference between the true pressure on the sample and the applied pressure or what is often referred to as the “nominal” pressure. The friction effect was a much discussed topic in the early stages of piston-cylinder experiments (e.g., Johannes *et al.*, 1971) and does not seem to have been properly appreciated even today. To address the problem, George Kennedy and his group at UCLA explored the behaviour of different types of pressure cells and came up with what is now known as “salt pressure cells” for effectively frictionless experiments in the piston-cylinder apparatus (e.g., Mirwald *et al.*, 1975). (In this type of pressure cell, which is now being widely used, the exterior bushing that insulates a graphite internal resistance furnace from the cylinder wall, as well as some of the internal parts within the furnace are made of pre-compressed salts like NaCl, KBr, CsCl that have very little shear strength at high temperature).

Many years after I moved to the University of Arizona, I got one of my graduate students, Kunal Bose, interested (another way of saying coerced) to determine the quartz-coesite transition boundary involving a thorough investigation of the friction behaviour of a salt cell. Here the seemingly “wasteful” segment of my years in Kennedy’s lab – see Section 1.4.3 – working on determination of the melting temperature of metals as a function of pressure by *in situ* DTA experiments and detecting phase transformations in alcohol from the relationship between pressure and piston displacement in a piston-cylinder apparatus came in handy. It was found that initially the friction in a salt cell was as high as 6-7 % of the nominal pressure but it decayed to effectively zero after ~25-35 hr, in ½” – ¾” diameter pressure cells at ~875 °C (the rate of friction decay should increase with increasing temperature because of the decrease of shear strength of the pressure cell). The experiments for quartz-coesite transitions were run for greater than these threshold durations to ensure that the final nominal pressure equalled the sample pressure. The experimental results (reversal brackets, the equilibrium boundary and friction decay) are illustrated in Figure 3.1. A thorough analysis of the friction behaviour of a salt cell as a function of time, temperature, rate of pressurisation and the diameter of the pressure cell was presented in the paper by Bose and Ganguly (1995). Here I take the opportunity to reiterate a point that we made in our paper but probably with little effect. The common practice of maintaining a fixed nominal pressure by repeatedly pressurising the cell during an experiment leads to progressive increase of sample pressure instead of the desired outcome of the procedure of maintaining a fixed sample pressure.



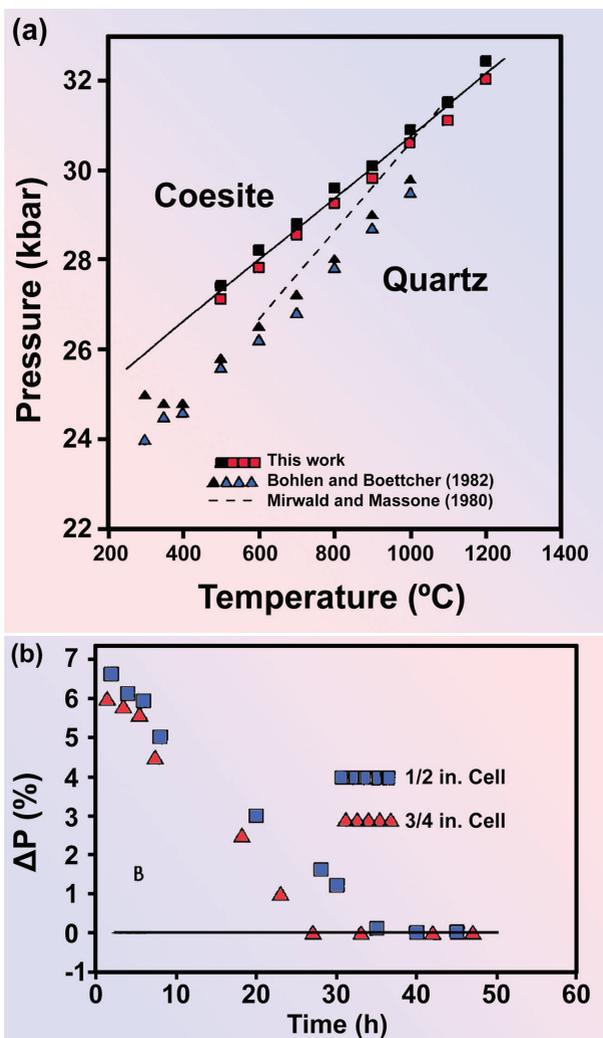


Figure 3.1

(a) a-quartz-coesite transition determined by frictionless reversed experiments in a piston-cylinder apparatus (squares) and comparison with the data of Bohlen and Boettcher (1982: triangles) and Mirwald and Massone (1980: dashed line). Black and coloured symbols: growth of coesite from quartz and vice-versa, respectively; solid line: the calculated equilibrium boundary using the enthalpy of formation and entropy of coesite retrieved from the experimental data. (b) Rate of friction decay in a salt pressure cell (1/2" and 3/4" diameters); ΔP (%) represents the percentage deviation of the nominal pressure from the true pressure. Modified from Bose and Ganguly (1995). (The Bose and Ganguly data seem to have become a benchmark set for the determination of friction in piston-cylinder experiments)



For an exchange reaction a reversal bracket for $K_D(i-j)$ at a fixed P-T-X condition consists of a pair of closely spaced values, which have been obtained from crystalline starting mixtures that were initially at the higher and lower K_D sides of the anticipated equilibrium value. This approach is illustrated in Figure 3.2, which consists of Roozeboom plots for the Fe-Mg binary systems in (a) spinel-orthopyroxene (Liermann and Ganguly, 2003), and (b) olivine-orthopyroxene (von Seckendorff and O'Neill, 1993) systems (note the similarity in the forms of Fig. 3.2b and Fig. 2.1b). As opposed to this protocol, there are many studies in which $K_D(i-j)$ -s had been determined from the synthesis experiments using glass starting material. For the reasons discussed above, there is no guarantee that the reported $K_D(i-j)$ values obtained from this type of experiments tightly constrained the equilibrium values. In some cases, attainment of equilibrium had been claimed by time series experiments when there was no change of the mineral compositions with time. Such steady state results constitute permissive but not definitive evidence of attainment of equilibrium composition.

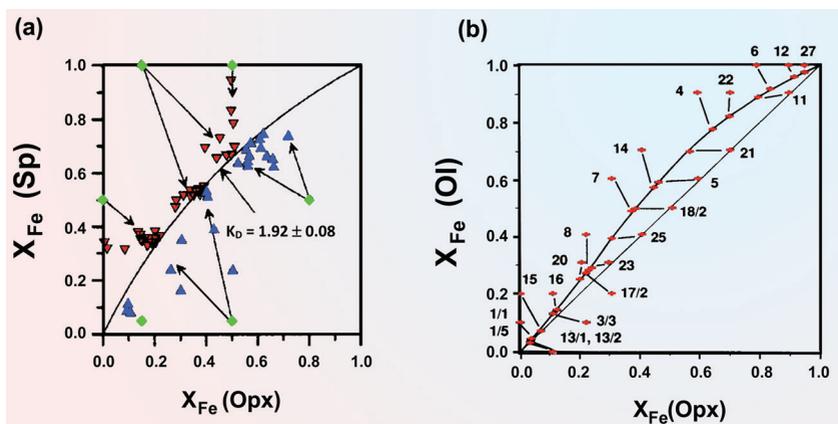


Figure 3.2 Equilibrium fractionation of Fe²⁺ and Mg between (a) spinel and orthopyroxene (T = 1000 °C, P = 9 kbar) and (b) olivine and orthopyroxene (T = 1000 °C, P = 16 kbar) as determined experimentally by Liermann and Ganguly (2003) and von Seckendorff and O'Neill (1993), respectively. In (a), the initial compositions are shown by filled diamond symbols and the evolved ones by triangles. The most evolved compositions can be fitted well by a constant distribution coefficient, K_D , which describes a symmetric curve. In (b), the initial compositions are numbered and connected to the evolved compositions by lines. The equilibrium distribution curve is asymmetric which implies that K_D depends on Fe²⁺/Mg ratio. In both sets of experiments, the equilibrium distribution is constrained by reversal experiments.

For determining the equilibrium composition of a mineral in a divariant reaction, such as the composition of garnet in the GASP reaction (2.3), one has to bracket it by using two types of starting mixtures of reactant and product in which the mineral composition is on two sides of the anticipated equilibrium



composition and follow their evolution. This procedure, which is analogous to that recommended for exchange equilibria, is illustrated for the specific case of the grossular content of garnet in the GASP reaction in Figure 3.3.

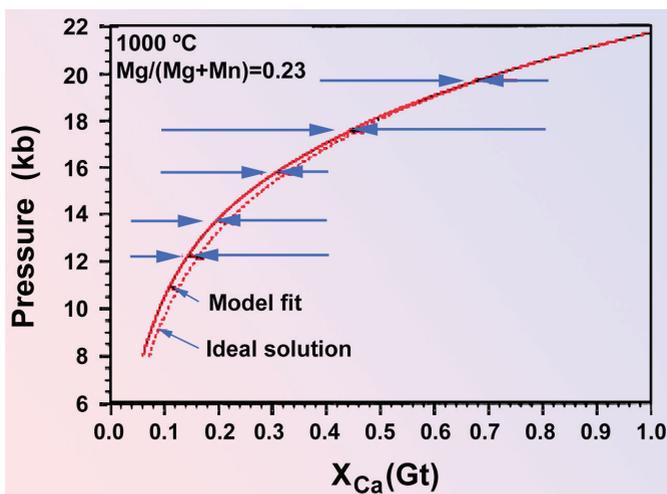


Figure 3.3 Experimentally determined effect of composition on the GASP equilibrium in the ternary system Ca-Mg-Mn at 16 kb, 1000 °C. The Mg/(Mg+Mn) ratio of synthetic garnet was kept constant at 0.23. The arrows show the direction of evolution of garnet compositions with the initial and final compositions being indicated, respectively, by the tail ends and the arrow heads. Modified from Ganguly *et al.* (1996).

3.2 Aluminum Silicate Phase Diagram and the 1969 Yale Conference

In the early phase of thermobarometry of metamorphic rocks, the stability relations of kyanite, sillimanite and andalusite became a hot topic since, according to the Gibbs Phase Rule, the coexistence of a pair of the polymorphs defines a line in the P-T space for the condition of metamorphism of the host assemblage. In addition, the coexistence of all three polymorphs was also reported from more than a dozen assemblages in regionally metamorphosed terranes around the world, leading to the exciting possibility of pinpointing their P-T conditions since, under equilibrium condition, the three polymorphs can coexist only at a point in the P-T space. Thus, there was a flurry of activity to determine the aluminum silicate phase diagram in different laboratories that had facilities for high P-T experiments and/or determination of thermodynamic properties of minerals. And when I was in the final stretch of my dissertation research at Chicago, Bob Newton got into the act and produced the first set of reversed experimental data to constrain the metastable extension of the kyanite/andalusite boundary in



the sillimanite field. Figure 3.4 shows the aluminum silicate phase diagram of Newton (1966), along with those by others as summarised by him, that should give an impression of the state of the mess.

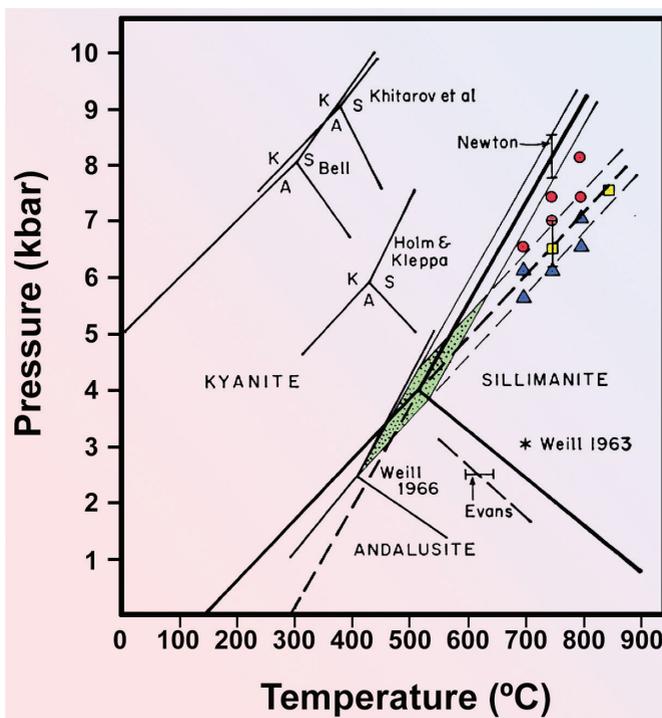


Figure 3.4

Aluminum silicate phase diagram by different workers, as compiled by Newton (1966) and referenced therein. The experimental reversal of the metastable extension of the kyanite-andalusite boundary by Newton (1966) are shown by red circles and blue triangles that indicate, respectively, growth of kyanite at the expense of andalusite and vice-versa. The yellow squares indicate no reaction. The phase diagram developed by him is shown by heavy lines along with an error envelope (stippled area) around the triple point. Modified from Newton (1966).

The large disagreements among the results from different laboratories led to a pessimistic feeling about whether the phase relations of the aluminum silicate polymorphs could be determined in the laboratory at all and also about possible unknown effects on the thermodynamic properties of the polymorphs that could have affected their stability relations in the natural assemblages. A small international conference was convened at the Kline Geology Laboratory of the Yale University in 1968, when I was a post-doc there, to address the problem of "A disturbingly large uncertainty in the position of the triple point, combined with



inabilities of different investigators satisfactorily to explain the discords ...". The quote is from the Preface by Brian Skinner of a special volume of the *American Journal of Science* (1969) that was devoted to the publication of papers submitted by many of the participants in the conference. As stated by Skinner, to “*keep discussions open and frank, publication of papers presented was not required.*” The wide scatter in the experimental data on the aluminum silicate phase diagram seemed to have resulted from a variety of problems such as metastable persistence of the phases beyond their fields of thermodynamic stability stemming from the small free energy difference between the polymorphs, preferential increase of the overall free energy of kyanite relative to sillimanite upon intense grinding *etc.*

After listening to the presentations and intense discussions that followed during the formal sessions and spilled over to the coffee and socialisation breaks, I felt that one should investigate if there were some constraints imposed by other systems on the location of the aluminum silicate triple point. I was then writing my paper on chloritoid stability (Ganguly, 1969) and thus decided to have a close look at the association of chloritoid with the aluminum silicate polymorphs in the natural assemblages. This exercise led me to conclude that the triple point should be located between the equilibria $\text{Chd} + \text{Al}_2\text{SiO}_5 = \text{St} + \text{Q} + \text{H}_2\text{O}$ and the upper stability limit of chloritoid in order to be compatible with the observational data (in natural rocks, it is either kyanite or andalusite that coexists with chloritoid plus staurolite and but in the absence of staurolite, chloritoid sometimes coexist with sillimanite). Figure 3.5 shows the locations of the triple point, as determined by several workers, in relation to those of the two bounding reactions. The limiting P-T trajectory of the equilibria were calculated from the experimental data in the end member systems (Richardson, 1968; Ganguly, 1969) such that there was the widest gap between them after accounting for the compositional effects in natural assemblages.

Based on the above logic and calculations, I suggested that the aluminum silicate triple point should be located within the range of 3.5 to 5.5 kb and 500 to 570 °C that defined a small field of experimental data within the bounding chloritoid reactions. Only two experimental determinations, the one by Newton (1966) and the other by Richardson *et al.* (1969), fell within the defined limits but the latter very marginally so considering its error envelope. The data of Holdaway (number 7), who eventually presented a widely accepted phase diagram for the aluminum silicate polymorphs based on thorough experimental study and thermodynamic analysis, was way off the suggested range. His revised determination of the triple point at 3.76 kb -501 °C) that was published a couple of years later (Holdaway, 1971) fell just within the range.

I was teaching in a Chemistry department in a remote area in India (see Section 1.4.2) with absolutely no connection to the world of Geology when Holdaway’s paper came out. I became aware of this important contribution after I returned to USA in the mid-1972 and was happy to see that Holdaway had made the “cut” after a rough start, even if that was by one degree and 100 bars! The



triple point calculated from the internally consistent data bases of Berman (TWQ programme package) and Holland and Powell (THERMOCALC programme package) are at ~3970 bars, 510 °C and ~3750 bars, 508 °C, respectively.

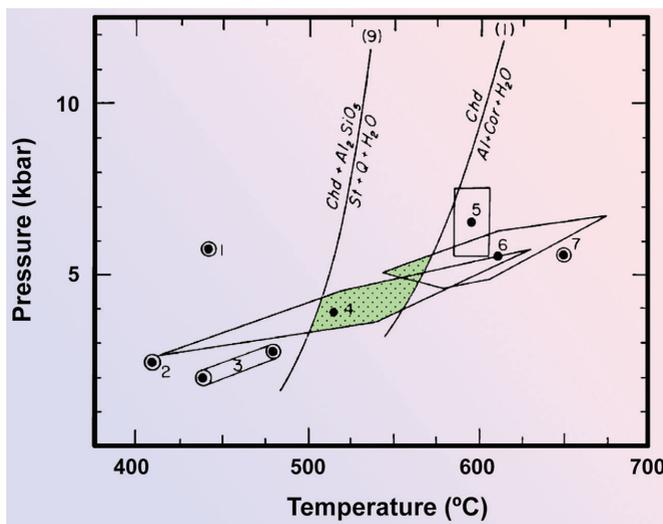


Figure 3.5 The aluminum silicate triple point, as determined by different workers (numbers) that were compiled by and referenced in Ganguly (1969), along with the locations of two chloritoid breakdown reactions. The line for the reaction (9) $4 \text{ Chd} + 5 \text{ Al}_2\text{SiO}_5 = 2 \text{ St} + \text{Q} + 3 \text{ H}_2\text{O}$ shows its lowest thermal limit and that for (1) $3 \text{ Chd} = \text{Alm} + 2 \text{ Cor} + 3 \text{ H}_2\text{O}$ shows its highest thermal limit, as calculated from experimental data accounting for the compositional effects in geological environments. 1- Holm and Kleppa (1966); 2 - Weil (1966); 3 - Fyfe (1967); 4 - Newton (1966); 5 - Althaus (1967); 6 - Richardson *et al.* (1969); 7 - Holdaway (1968). The enclosed areas around 3-6 represent the uncertainties of the respective determinations. The stippled area defines a condition within 3.5-5.5 kb and 500-570 °C for the correct location of the triple point. Modified from Ganguly (1969).

Subsequent to Ganguly (1969), there have been two more studies on the location of the aluminum silicate triple point using phase equilibrium constraints from natural assemblages, one by Greenwood (1976) and the other by Pattison (1992). Considering the fibrolitic variety of sillimanite, Greenwood (1976) located the triple point at ~4.75 kb, 575 °C, whereas, based on a study of phase equilibrium relations in the Ballachulish aureole, Scotland, Pattison (1992) suggested that the triple point is located at 4.5 (± 0.5) kb, 550 (± 35) °C. The latter is roughly around the middle of the range constrained by Ganguly (1969); however, considering the error bar, the upper temperature limit overshoots the constraint by 15 °C.



At this point, the history behind the publication of my paper on chloritoid stability may be worth recollecting. I initially submitted the paper to *Geochimica et Cosmochimica Acta*, but it was almost immediately rejected by the Executive Editor (EE) saying that the subject matter of the paper was not suitable for the journal. After receiving the rejection, I walked down to the office of the *American Journal of Science* (AJS) – located one floor below mine in the Kline Geology Lab – and submitted the paper in person without the formality of a cover letter. The next day Karl Turekian, who was a professor at Yale and a member of the editorial board of GCA, dropped by my office and told me that he had received a copy of the rejection letter of my paper and asked if I agreed with the reason for the rejection. My response was an emphatic no, and I also told him that the reason that I had submitted the paper to GCA was that Hugh Greenwood was an associate editor of the journal and I wanted to have the benefit of his comments since this paper would most certainly have been assigned to him for editorial handling, if it were not rejected by the executive editor. Greenwood's specialty was experimental and theoretical petrology and so I further added that if the subject matter of my paper was not suitable for GCA, then I had no clue what Greenwood's role was as a member of the editorial board. About a week or so later, I got a letter from Greenwood requesting me to send him a copy of my paper, which I did right away. This was obviously prompted by Turekian's action within the editorial board. After some time, Greenwood wrote to me saying that he was sorry that the paper was rejected by the EE and the decision would have been otherwise if he had the opportunity to see it earlier.

One notes in the *Geochemical Society News* (1970, No. 51), which was made available to me by the current EE, Jeff Catalano, that a survey was conducted by the Council members asking the society members to indicate their interests among seven broad fields and that "Experimental Petrology-phase equilibria (including hydrothermal)" received the second highest score. The same issue also shows that the EE tendered his resignation in 1970 after completion of one year of his three year term. No reason was given but it seems quite likely that this was precipitated by the dissatisfaction of the members of the editorial board about his editorial handling of papers, especially in the area of experimental petrology, and the result of the survey. At any rate, my paper sailed through the review process in AJS, and also caught Greenwood's attention that may be appreciated by reading his outstanding paper on the buffering mechanism of pore fluids by metamorphic reactions (Greenwood, 1975), as well as his review article on metamorphism at moderate P-T conditions (Greenwood, 1976). (In the first one, Greenwood sought to explain the observed regularity in the spatial distribution of minerals, such as in a Barrovian sequence, despite the complications in the phase relations of iron-bearing minerals resulting from variation of $f(\text{O}_2)$ (Ganguly, 1969; Eugster and Wones, 1962) and of hydrous and carbonate minerals due to variation of fluid composition (Greenwood, 1967). He concluded that the repetitive patterns of spatial distribution of minerals were due to the buffering of the fluid compositions caused by certain types of metamorphic reactions.)



3.3 Peridotite Phase Relations and the 1975 Thermobarometry Conference at Penn State

Natural orthopyroxene (Opx) may contain a significant amount of Al_2O_3 in solid solution, up to ~10 wt. %, depending upon the nature of coexisting phases and P-T condition at which the mineral assemblage equilibrated¹⁵. It was recognised by several researchers in the 1970s that alumina content of Opx could be used for thermobarometry of mantle xenoliths. The first comprehensive experimental study of the phase relations showing the spinel to garnet peridotite transition and alumina isopleths in enstatite (En) in the assemblages of forsterite (Fo) plus spinel (Sp) or garnet (Grt) in the simplified mantle system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS) was due to MacGregor (1974). The results were based on mixtures of crystalline starting materials for experiments related to the determination of the phase boundary and glasses of appropriate compositions for those related to the determination of the isopleths.

The MAS phase diagram of MacGregor (1974), which is reproduced as Figure 3.6a, shows two fields: En + Fo + Sp on the left and En + Fo + Grt on the right, with the lighter solid and dashed lines indicating alumina isopleths in enstatite within the two fields. An obvious problem with this phase diagram is the fact that the alumina isopleths hardly show any change of slope across the phase boundary of spinel to garnet bearing assemblages ($4\text{En} + \text{Sp} \leftrightarrow \text{Pyr} + \text{Fo}$). The T-P slope of an isopleth is governed by the Clayperon-Clausius relation, $dT/dP = \Delta V/\Delta S$, where ΔV and ΔS are, respectively, the volume and entropy changes of the reactions $\text{Pyr} = \text{Mg-Ts} + 2\text{En}$ in the pyrope field and $2\text{En} + \text{Sp} = \text{Mg-Ts} + \text{Fo}$ in the spinel field (in terms of the Opy component discussed in the footnote 15, the reactions are $\text{Pyr} = \text{Opy}$ and $\text{En} + \text{Sp} = \text{Opy} + \text{Ol}$). Even without going into detailed thermodynamic analysis, one should find it to be very unlikely that $\Delta V/\Delta S$ ratios of two such different reactions would be almost the same. The decisive step to address the problem was taken almost simultaneously by Wood (1975a) and Obata (1976). They calculated the phase diagram for the MAS system and showed that if one accepts McGregor's data for the alumina isopleths in the pyrope field, then those in the spinel field should have quite gentle (positive) T-P slopes and that the phase boundary should have a strong curvature that is convex toward the T-axis. They chose to accept the isopleth data in the pyrope field instead of that in the spinel field since there were major discrepancies between the spinel field data of MacGregor and others (see Obata, 1976, for further discussion), although none of the latter was definitive. In his study, MacGregor (1974)

15. It was shown by Ganguly and Ghose (1979) based on crystal chemical and structural arguments that 25 mol % is the upper limit of alumina substitution in enstatite. They, thus, suggested that a component $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ($3\text{MgSiO}_3 + 1\text{Al}_2\text{O}_3$) with an orthorhombic structure, which they called orthopyrope (Opy), should be taken as the end member component of Al-En instead of the commonly used $\text{MgAl}_2\text{SiO}_6$ component (Mg-tschermak: Mg-Ts that has 50 mol % alumina), and demonstrated that this change of strategy leads to closer approach to ideal solution behaviour of the aluminous enstatite solid solution.



discussed the possibility of a flatter dT/dP slope of the alumina isopleths in the spinel field and a curvature of the phase boundary but decided to settle for a straight phase boundary since it provided the best fit to his experimental data, and also in favour of his own isopleth data.

In 1975, an International Conference on Geothermometry and Geobarometry that I attended was organised in the Pennsylvania State University. This was the first such conference in the “teething” period of the field. In my recollection, the peridotite phase diagram in the MAS system was the most discussed topic in that conference because of the conflicting nature of the diagrams presented by McGregor (1974) and Wood (1975a). The results of Obata’s (1976) paper referred to above followed this conference. He was apparently unaware of the work done by Wood who also attended the conference and perhaps drew the most attention.

In collaboration with late Subrata Ghose (Fig. 2.2), I carried out a detailed study of the intra-crystalline distribution of Al in synthetic Al-En crystals by X-ray diffraction and deduced the entropy and volume of Al-En solid solution as a function composition and temperature. These data enabled calculation of the dT/dP slope of aluminous isopleths in the spinel field and indeed the slopes turned out to be quite flat. Later, I gave an oral presentation on this in a GSA meeting that was followed by a presentation by Ian MacGregor on a different topic. After MacGregor’s talk, someone from the audience stood up and asked MacGregor to explain his results on the alumina isopleths in the spinel field instead of asking a question on his talk (in my recollection, that person was David Eggler, at that time a rising star in the field of experimental petrology).

Subsequently, we undertook a project to determine the aluminum solubility in enstatite in equilibrium with pyrope using reversed experimental protocols and crystalline starting mixtures (see Section 3.1) to unambiguously constrain the equilibrium solubility. Using thermodynamic analyses of these data and those of a limited set of reversed alumina solubility data of Danckwerth and Newton (1978) in the spinel field, the available data on the heat capacity and compressibility of minerals, we calculated the phase diagram in the MAS system showing the univariant phase boundary and the alumina isopleths (Lane and Ganguly, 1980). These calculations required some optimisation of the thermodynamic properties retrieved from the experimental data on the isopleths and development of methods for extrapolation of C_p and compressibility data beyond their P-T domains of measurements obeying thermodynamic constraints. The extrapolations methods are now much discussed topics in the development of thermochemical databases in the geological community (see for example, Ganguly, 2020). The phase diagram calculated by Lane and Ganguly (1980), which is reproduced as Figure 3.6b, showed remarkable agreement with the reversed experimental data of Danckwerth and Newton (1978) for the spinel- to garnet-peridotite transition in the MAS system.



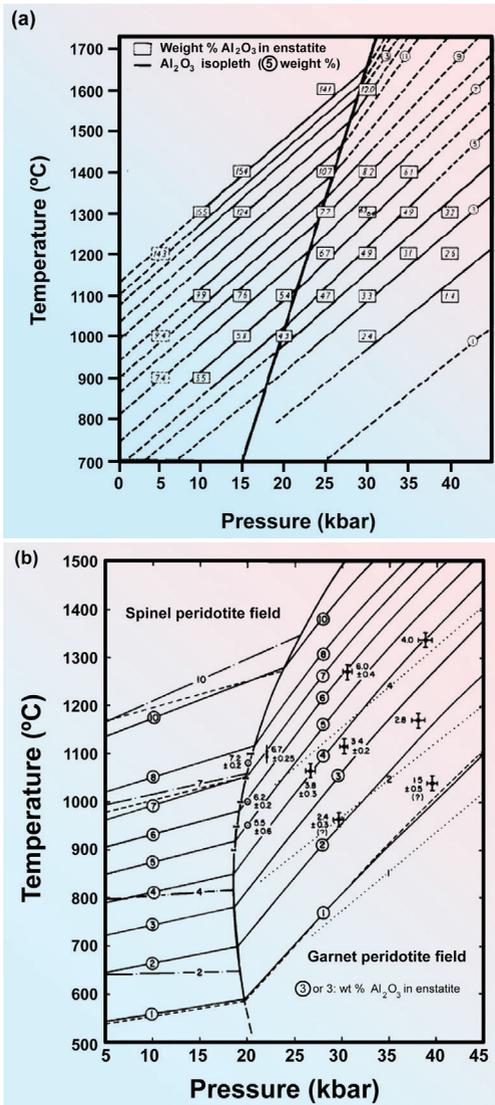


Figure 3.6

Spinel-peridotite to garnet-peridotite transition in the MAS (MgO-Al₂O₃-SiO₂) system, along with alumina isopleths in enstatite. **(a)** Experimental determination by MacGregor (1974). **(b)** Calculated diagram by Lane and Ganguly (1980) using reversed alumina solubility data in enstatite in the garnet field, as determined by them (crosses), and in the spinel field, as determined by Danckwirth and Newton (1978).



Text Box 3.2 – Peridotite phase relations and G-minimisation method for phase equilibrium calculations

In 1983, Saxena and Eriksson published a set of three papers on phase equilibrium calculations that mark the beginning, at least to my knowledge, of the calculation of phase equilibria in natural systems using the method of Gibbs free energy minimisation at specified P-T conditions; this method has now been incorporated in several widely used computational programme packages such as those discussed in Section 4.2. The paper by Saxena and Eriksson (1983) specifically dealt with the peridotite phase relations in the multicomponent systems, MAS plus additional components, that adequately capture the compositions of the mantle derived rocks. The calculations were carried out by first creating an internally consistent thermodynamic database of the minerals found in the mantle rocks and then using those data in a G minimisation scheme to calculate the phase diagrams including Al-isopleths in orthopyroxene and modal abundance of the phases, the latter being a completely new feature in phase equilibrium studies. Similar calculations can now be carried out using the more updated databases described in Section 4.2 and different strategies for the minimisation of G, but the work of Saxena and Eriksson (1983) marks the beginning of this important field. (In creating the thermodynamic database for the mantle minerals, Saxena and Eriksson (1983) considered all reliable experimental data on the alumina isopleths in orthopyroxene in the MAS (e.g., Fig. 3.6b) and CMAS systems. Their calculated isopleths match these experimental data within the range of their uncertainties.)



4.1 Multi-reaction Topologies: Fixed Mineral Compositions

The idea of the petrogenetic grid of Bowen (1940) that was developed in connection with his decarbonation series of siliceous limestones and dolomites probably constitutes the earliest quantitative approach to constraining the P-T condition for equilibration of an observed mineral assemblage in a rock. A very important step towards the development of the petrogenetic grid is due to Korzhinskii (1959), who adapted Schreinemakers' principles of organising a set of univariant reactions intersecting at an invariant point in a self consistent way (see, for example, Niggli, 1954; Ganguly, 2020 for an exposition of Schreinemakers' principles) to systems involving two or more invariant points; these systems are those that have more phases than required to define an invariant point, according to the Phase Rule. This type of geometrical analysis has been commonly referred to as multi-bundle Schreinemakers' analysis. Korzhinskii also developed a matrix method of writing balanced chemical reactions that emanate from each invariant point in a system.

Albee (1965), Ganguly (1968, 1969, 1972) and Hensen and Green (1973) were the earliest in the English literature to use Korzhinskii's method of multi-bundle Schreinemakers' analysis to develop petrogenetic grids. While Albee's was a geometric analysis with the slopes of univariant reactions constrained from thermodynamic considerations, the others quantified the grids by carrying out critical experimental studies. Ganguly (1972) presented the phase relations of Fe-staurolite in the P-T- $f(\text{O}_2)$ space and for its limiting compositions in natural assemblages (Figs. 4.1, 4.2). The Figure 4.1 shows the multi-bundle phase diagram in the T- $f(\text{O}_2)$ space at a constant pressure of 5 kb, whereas the Figure 4.2 shows a P-T section at $f(\text{O}_2)$ defined by the Ni-NiO buffer; the latter also shows the limiting solid solution effects in common pelitic bulk compositions that were calculated from thermodynamic analysis of the mineral equilibria. As an example of this type of calculation, consider the reaction $6\text{Fe-St} + \text{Qtz} = 4\text{Alm} + 23\text{Ky} + 3\text{H}_2\text{O}$. At a constant temperature, the displacement of equilibrium pressure of this reaction with respect to the experimentally determined pressure (P_{ex}) in the pure iron bearing system is given by the relation (Ganguly, 1972)

$$P - P_{\text{ex}} = \frac{3}{\Delta V^{\text{s}}} \left[G^{\text{H}_2\text{O}}(P_{\text{ex}}, T) - G^{\text{H}_2\text{O}}(P, T) - 4(2.303)RT \log K_X^{\text{G-S}} \right]. \quad (4.1)$$

where ΔV^{s} is the solid volume change of the reaction, assumed to be independent of pressure, $G^{\text{H}_2\text{O}}$ is the Gibbs free energy of pure water, and $K_X^{\text{G-S}}$ is the ratio $X_{\text{Fe}}(\text{St})/X_{\text{Fe}}(\text{Grt})$. The complementary relation for calculating thermal displacement at constant pressure is given in Ganguly and Saxena (1987, their equation 4.48).



The lines with arrows in Figure 4.1 show geologically effective T- $f(\text{O}_2)$ paths in metapelites. At $f(\text{O}_2)$ buffered by the presence of graphite, there would be a well defined staurolite isograd where the mineral had formed from the thermal breakdown of chloritoid or chlorite (the chloritoid-staurolite and chlorite-staurolite reactions take place at similar temperatures) and followed by the aluminum silicate isograd (kyanite or sillimanite, depending on the pressure: see Fig. 4.2; kyanite appears before sillimanite above 7 kb). However, in the absence of graphite, the $f(\text{O}_2)$ could rise to the upper end of the magnetite field leading to the appearance of kyanite or sillimanite instead of staurolite at temperatures where the latter would be found in volumes of rock with lower $f(\text{O}_2)$ conditions.

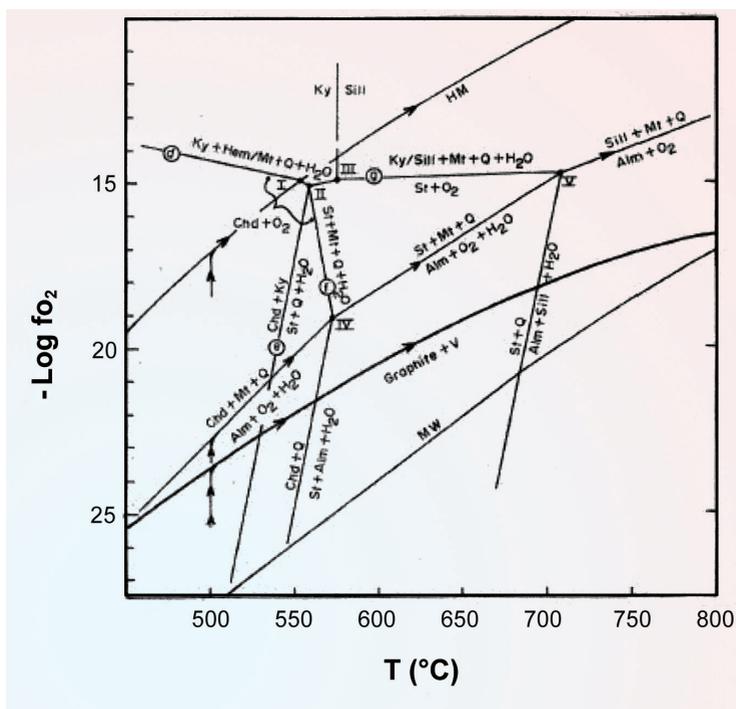


Figure 4.1

A quantitative multi-bundle Schreinemakers' diagram depicting the phase relations of chloritoid (Chd), staurolite (St), almandine (Alm), aluminum silicates (Ky: kyanite; Sill: sillimanite) and iron oxides along with graphite – C-O-H ($\text{H}/\text{O} = 2$) buffer in the T- $f(\text{O}_2)$ space at 5 kb pressure in the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}_2\text{-O}_2$ (FASHO). The triangular field in the middle defines the stability of the assemblage staurolite + magnetite + quartz. MW and HM: Magnetite-wüstite and hematite-magnetite buffers, respectively. Arrows: paths of geologically effective $f(\text{O}_2)$ buffers. Graphite-vapor equilibrium is after French (1966). Modified from Ganguly (1977) which based on data of Ganguly (1972) that also shows a 10 kb section.



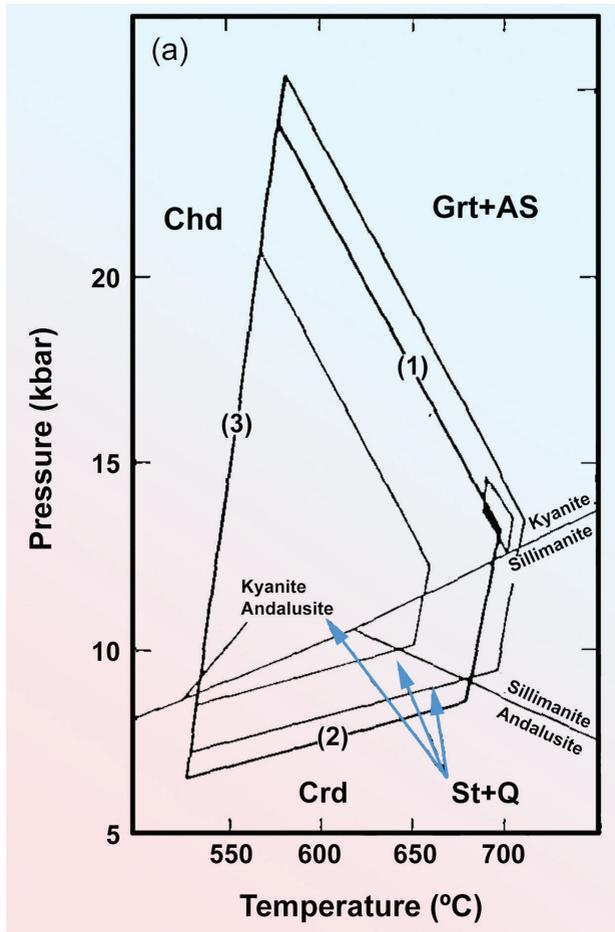


Figure 4.2

P-T stability limits of staurolite at $f(\text{O}_2)$ defined by the Ni-NiO buffer. Heavy (numbered) lines denote the stability limits of Fe-staurolite, whereas the lighter lines denote the stability for the limiting staurolite compositions in the common metapelitic rocks. The reactions along with compositions of solid solutions for the light lines are as follows: (1) $\text{St} + \text{Qtz} = \text{Grt} + \text{AS} + \text{H}_2\text{O}$: uppermost line: $X_{\text{Fe}}(\text{Grt})/X(\text{St}) = 1.1$, lowermost: $X_{\text{Fe}}(\text{Grt})/X(\text{St}) = 0.7$; (2) $\text{St} + \text{Qtz} = \text{Crd} + \text{AS} + \text{H}_2\text{O}$: uppermost: $X_{\text{Fe}}(\text{Crd})/X(\text{St}) = 0.30$, lowermost: $X_{\text{Fe}}(\text{Crd})/X(\text{St}) = 0.38$; (3) $\text{Chd} + \text{AS} = \text{St} + \text{Qtz} + \text{H}_2\text{O}$, which is insensitive to compositional effects. The open quadrilateral: Uncertainty in the intersection of the staurolite plus quartz stability limits in the kyanite and sillimanite fields. The divariant P-T regime defined by the light lines for the equilibrium (2) consists of the assemblage St + Crd that characterizes the "Buchan type" intermediate pressure metamorphic facies series. Modified from Ganguly (1972).



The domain defined by the two lighter lines of reaction (2) in Figure 4.2 constrains the metamorphic P-T field gradient of the Buchan-type regional metamorphism in pelitic rocks that is characterised by the coexistence of staurolite and cordierite (a metamorphic field gradient is the locus of peak temperature and the associated pressure experienced by the rocks of different grades; it is, in general, different from a steady state geotherm). The equilibrium (3) defining the transition from chloritoid (Chd) to staurolite (St) turned out to be insensitive to solid solution effects owing to the nearly equal fractionation of Fe^{2+} between the two phases (*i.e.* $K_x^{\text{Chd-St}} \approx 1$). Allowing for the effects of changing volatile composition ($X(\text{H}_2\text{O}) < 1$), the conditions defined by the equilibria (3) and (1) (the two lines for the latter mark, respectively, the condition of the classic staurolite and kyanite isograds in the Barrovian metamorphism, the development of which require $f(\text{O}_2)$ buffering of pore fluids around the middle of the magnetite field by graphite or mineral reactions (Greenwood, 1975; Ganguly, 1977).

The $f(\text{O}_2)$ controlled experiments at high pressure related to the determination of the stabilities of chloritoid and staurolite were the first such experiments and posed a major technical challenge. The details of the configuration of the sample capsules within a pressure cell are given in Ganguly and Newton (1969). The $f(\text{O}_2)$ buffering method was an adaptation of the pioneering study of Eugster and Wones (1962) on the stability relations of annite but making water tight seals of short capsules and retaining water in both sample and surrounding solid buffer capsules at the experimental P-T-t conditions posed major technical hurdles and led to heart breaking experience when a quenched sample plus buffer capsule turned out to be dry after an experiment.

4.2 Multi-reaction Topologies: Fixed Bulk Compositions

Hensen and Green (1973) presented a detailed analysis of the phase relations of cordierite and garnet in two fixed pelitic bulk compositions in the P-T space (Fig. 4.3). By comparing the inferred phase relations with some reported natural assemblages, especially those containing sapphirine plus quartz, this study made the important discovery that “In rare occasions temperatures of 950-1000 °C appear to have been reached during granulite metamorphism.” This led to the development of the field of ultra-high temperature (UHT) metamorphism that has since been discovered in a number of pre-Cambrian terranes (*e.g.* Philpotts and Ague, 2009: their Fig. 16.10).

A major advancement in the direction of calculating quantitative multi-bundle petrogenetic grids at fixed bulk compositions came through the computer based calculations of what are commonly referred to as pseudosections, in which the stable mineral assemblages are calculated at specified P-T condition and bulk composition, using an internally consistent thermodynamic database (I have never appreciated the name since I do not find anything to justify the “pseudo” qualification). The qualification “internally consistent” implies mutual compatibility of the Gibbs free energy values of the phases so that the phase equilibrium



calculations reproduce experimentally determined phase diagrams that were chosen to retrieve the thermodynamic properties of the phases, along with other types of data. This, however, does not guarantee accuracy of the thermodynamic properties (enthalpy, entropy, heat capacity, thermal expansion, compressibility) that have been combined to calculate the free energy at a given P-T condition. This type of calculation was a vision of Harold Helgeson who took the first major step toward that goal by developing an internally consistent thermodynamic database of rock forming minerals (Helgeson *et al.*, 1978). He told me that sometime in the future, people should be able to calculate phase diagrams of minerals by taking sections in the compositional space.

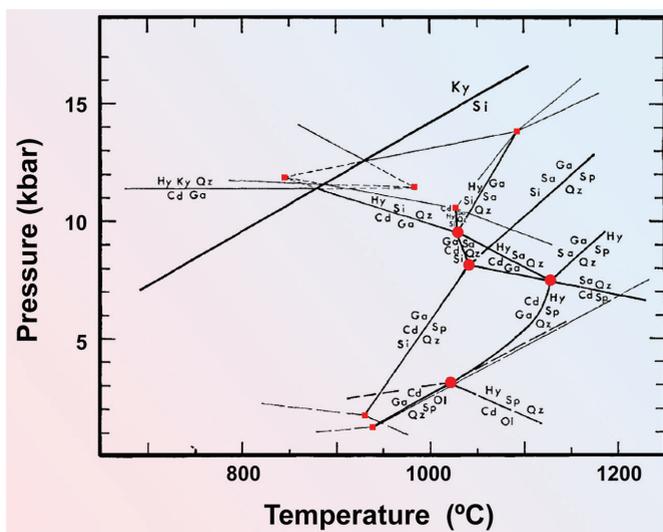


Figure 4.3 P-T diagram depicting the stability relations of cordierite (Cd), garnet (Ga), spinel (Sp) for two types of bulk compositions (heavy, and light lines) in the system FeO-MgO-Al₂O₃-SiO₂ (FMAS). Modified from Hensen and Green (1973).

The popularly used computer programmes for pseudosection calculations are Theriak-Domino (de Capitani and Brown, 1987), THERMOCALC (Holland and Powell, 1998) and Perple_x (Connolly, 1990, 2005). These software packages calculate the stable modal abundance and compositions of minerals by minimising the Gibbs free energy of the system, but using different computational strategies (*e.g.* see Ganguly, 2020). All use the internally consistent thermodynamic data base of Holland and Powell (1998) that is being updated as needed but the programme Perple_x gives additional flexibilities of using other databases, different solution models and equations of states that have been incorporated in its database files. All these programmes are available on-line. An example of pseudosection calculation using bulk composition of a natural rock is given in the



next section (Fig. 5.6). (It may be noted incidentally that free energy minimisation strategy has also been used in the MELT software package of Ghiorso and Sack for calculating melting and crystallisation behaviour of rocks; the programme package is available on-line.)

Text Box 4.1 – Thermodynamic database and phase equilibrium calculations: early effort using Bayesian statistics

In this context, it may be pointed out that more than 20 years ago, Chatterjee and co-workers (Chatterjee *et al.*, 1998) developed an internally consistent thermodynamic database consisting of 148 end members in a geologically relevant multicomponent system using Bayesian statistics. This database, which represents the introduction of the Bayesian method in petrology-geochemistry, has the unique feature, absent in any other thermodynamic database, of showing the statistical uncertainties of the retrieved values of enthalpy of formation and entropy of the phases. Chatterjee *et al.* (1998) also developed computational algorithm that calculates mineral equilibria with error bars on the univariant boundaries in the P-T, T-f(O₂), T-X(CO₂), P-X(CO₂) sections propagating the uncertainties in the linked database. Unfortunately, they did not pursue this work far enough, especially involving thermodynamic mixing properties of the phases, to achieve a level of completeness that is found in other databases, and as a consequence this important study did not catch on so well in the petrology community.



5.1 P-T-t Paths from Diffusion Kinetic Modelling

Although it is rarely practised, diffusion kinetic modelling of compositional zoning may in some situations yield P-T-t paths with little or no data from conventional thermobarometry; such constraints are nonetheless desirable in order to provide independent checks and simplify the modelling protocols. I discuss below two examples of such reconstruction of P-T-t paths from our work.

The first example is the low temperature P-T path of a sample from the High Himalayan Crystalline (HHC) schist in the Sikkim region of eastern Himalayas. Figure 5.1 shows a two stage exhumation path of the sample; a nearly isothermal exhumation from ~30 km to ~12 km, followed by slow exhumation with an average velocity (V_z) ~2 mm/yr. The compositional zoning of a garnet crystal in this rock that developed during cooling by cation exchange with an effectively semi-infinite reservoir of biotite of uniform composition has been illustrated in Figure 2.8. This zoning profile must have developed during the slow cooling episode since in the segment of very rapid exhumation there was effectively no change of the garnet composition at the interface with biotite (because of nearly isothermal condition) to drive the diffusion.

The higher pressure segment of the P-T path was constrained from thermobarometry of peak conditions¹⁶, based on a combination of GASP and Grt-Bt Fe-Mg exchange equilibria, and retrograde breakdown of garnet to spinel or cordierite ($\text{Alm} + 2 \text{Sill} = 3 \text{Spnl} + 5 \text{Qtz}$ and $5 \text{Alm} + 4 \text{Sill} + 5 \text{Qtz} = 3 \text{Crd}$) in adjacent samples that were inferred from textural observations. The P-T trajectories of these equilibria were calculated from their experimentally determined locations in the FeO-Al₂O₃-SiO₂ system and thermodynamic analysis of the compositional effects corresponding to the observed compositions of the natural samples.

Diffusion modelling of the retrograde zoning of the garnet grain (Fig. 2.9) yields a value of $8.18(10^{-9}) \text{ cm}^2$ for the integral $\int D(t)dt$. (For the non-specialists, this integral is the non-isothermal counterpart of $D\Delta t$ that one retrieves from modelling compositional zoning under isothermal condition or uses in the back of the envelope calculation $X \approx \sqrt{D\Delta t}$). By itself D is not a function of time but in a non-isothermal problem D becomes time dependent because of the dependence of T on t .) The only thermometric data used in this modelling was the

16. Modelling of the Z(depth) -T path followed by regionally metamorphosed rocks in the over thrustured regions shows that during exhumation, a parcel of rock follows a counter clockwise Z-T path in which the highest temperature is attained at a shallower depth than that from which the rock started to exhume. Thus, thermobarometric calculations for such rocks usually yield the peak T and P at the peak T.



peak temperature determined on the basis of garnet core and matrix biotite composition. The modelling of the retrograde zoning during cooling was based on the asymptotic T-t relation introduced in Section 2.4.1 (a computer code¹⁷ for this type of modelling is available at https://www.geo.arizona.edu/~ganguly/pub/REAZ_M). An important aspect of the value of $\int D(t)dt$ is that it is independent of the cooling model so long as the initial and boundary conditions remain the same and the fits to the observed compositional zoning are not significantly different.

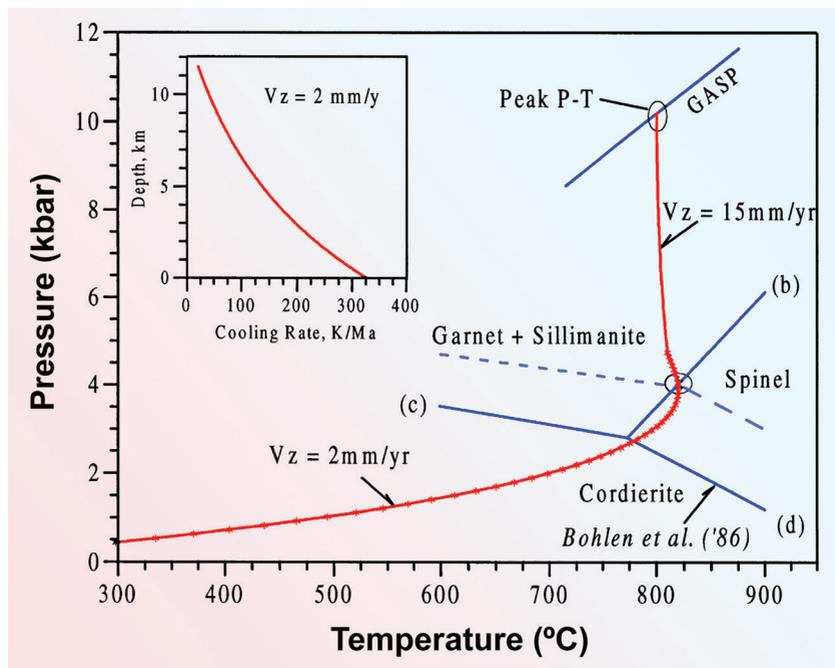


Figure 5.1 Two-step exhumation path and the corresponding exhumation velocities of a High Himalayan Crystalline (HHC) schist, as reconstructed from (i) thermobarometric calculations (Peak P-T) and textural observations of retrograde reactions plus related phase equilibrium constraints and (ii) diffusion kinetic modeling of retrograde zoning in garnet (Fig. 2.8). The inset shows the change of cooling rate as a function of depth for $V_z = 2$ mm/y. Modified from Ganguly *et al.* (2000).

17. This particular code enables modelling of the retrograde zoning profile developed by effectively binary Fe-Mg exchange between a garnet and a homogenous semi-infinite matrix. One can specify uncertainties in the input values of ΔH of the Fe-Mg exchange reaction, $D(\text{Fe-Mg})$ in garnet, initial composition in garnet and allow the interface to move (as would be case in a reaction-diffusion model). The diffusion modeling programme is interfaced with an optimisation routine that finds the best solution by varying the input parameters within the stated limits.



Now, the P-T-t path experienced by a parcel of rock exhuming at a prescribed velocity can be retrieved by solving the one dimensional heat conduction-convection equation involving radiogenic heat production in the medium. The solution of the equation for the simplified case of constant exhumation velocity, thermal diffusivity and heat production rate is given in Carslaw and Jaeger (1959, p. 388). Using this solution within a numerical scheme that permits stepwise variation of the heat production rate, the P-T-t path was calculated for a prescribed V_z . The corresponding $\int Ddt$ value was calculated from the T-t relation (that transforms $D(T)$ to $D(t)$) and compared with that obtained from the modelling of the retrograde zoning of the garnet crystal. The process was repeated until there was satisfactory match between the $\int Ddt$ values obtained from the two sources.

The coupled diffusion and heat transfer modelling resulted in the P-T path illustrated in Figure 5.1 with $V_z = 2$ mm/yr. It should be emphasised that the inferred P-T path is valid down to the temperature after which diffusion is too slow to have any significant effect on the compositional profile of garnet. This temperature was calculated to be ~ 450 °C based on the Grt-Bt Fe-Mg exchange thermometry using the rim composition of garnet and the composition of the biotite matrix that was found to be homogeneous within the scale of the thin section (satisfying the condition of homogeneous infinite matrix). (The exhumation velocity, $V_z = 15$ mm/yr, along the nearly isothermal path in the higher pressure segment was also calculated from the same heat transfer modelling protocol.)

Tirone and Ganguly (2010) modelled the compositional zoning of the major divalent cations (Fe, Mn, Mg and Ca) in garnets of different sizes from a suite of metapelites in a contact metamorphic terrane in the Ryoke metamorphic belt, Japan, to reconstruct the full T-t path (prograde, peak and retrograde) of the suite. The samples were initially studied by Okudaira (1996) who determined the major element zoning profiles in central sections of nearly spherical garnet crystals. The size difference among the garnets was considered to be related to the timing of garnet nucleation in the prograde path (the larger the size, the earlier is the time of nucleation). Tirone and Ganguly (2010) developed a finite difference programme for modelling the multicomponent diffusion profiles incorporating schemes for the development of prograde growth zoning and subsequent diffusive modifications at prograde, peak and retrograde thermal conditions, as well as nucleation and growth formalisms. This numerical code was interlinked with a genetic algorithm to handle several floating parameters and find the overall best match to the measured compositional profiles of Fe, Mn, Mg and Ca in five crystals varying in radius from 0.1 to 0.5 mm. The floating parameters were the growth constant, peak temperature (T_p), time to achieve T_p and the parameters governing the variation of surface concentration of three independent diffusing species (Fe, Mn, Mg) as function of temperature; Ca was treated as a dependent species obeying the stoichiometric constraint $X_{Ca} = 1 - (X_{Fe} + X_{Mn} + X_{Mg})$.



The simulated profiles are compared with the measured data in Figure 5.2 and the corresponding T-t path is illustrated in Figure 5.3. The latter also contains the T-t path calculated by Okudaira *et al.* (1994) and Okudaira (1996) from heat transfer modelling in the contact aureole. The agreement of these calculations of T_p and time to T_p with those retrieved from the diffusion kinetic modelling of garnet zoning profiles is noteworthy. The difference between the two sets of calculations in the cooling path is probably a consequence, at least partly, of the lack of sufficient spatial resolution of the measured data close to the edges that reflect the relatively lower temperature cooling rate.

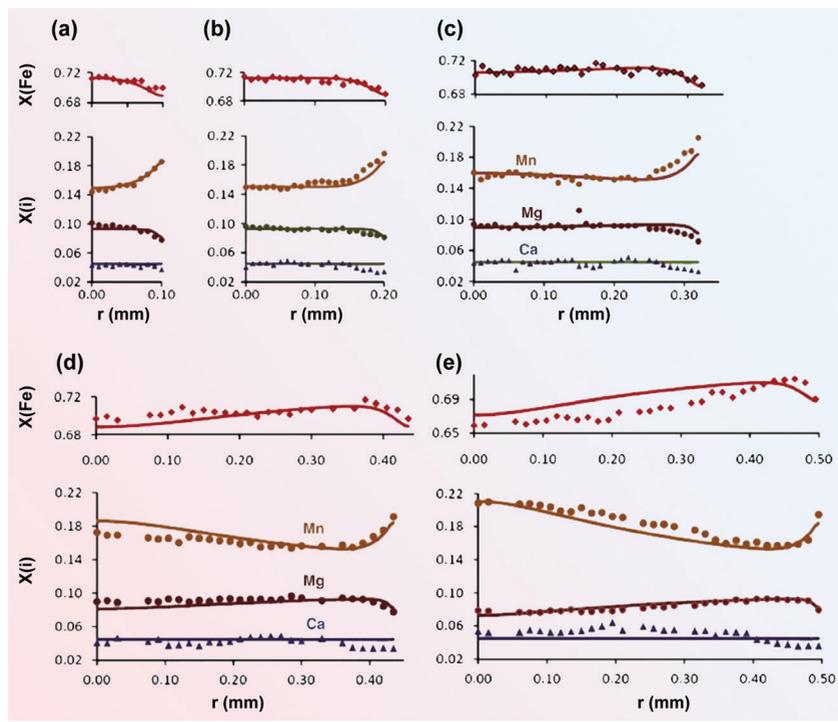


Figure 5.2 Numerical simulation (solid lines) and measured data (symbols) of the multi-component zoning profiles in garnet of different sizes (0.1 – 0.5 mm), assumed to have formed by a process of nucleation and growth along a prograde path in the low pressure-high temperature Ryoke metamorphic belt, Japan. The measured data are from Okudaira (1996 and pers. comm.). Modified from Tirone and Ganguly (2010).



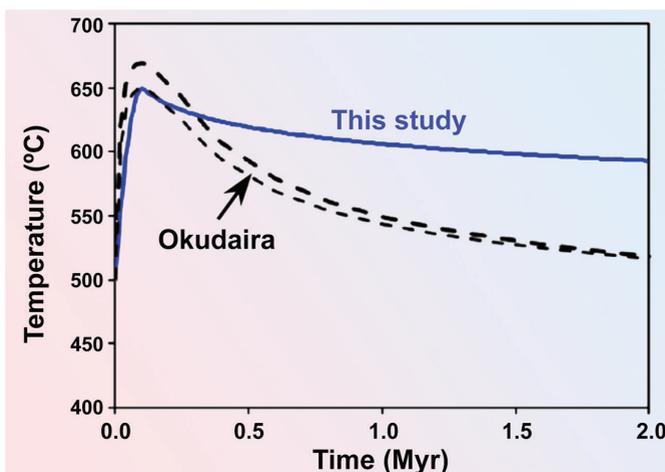


Figure 5.3 The T-t path, labeled as “This study”, corresponding to the successful simulation of the zoning profiles in garnet illustrated in Figure 5.2. The T-t paths constructed by Okudaira *et al.* (1994) and Okudaira (1996) from 1-D thermal modeling are illustrated, respectively, by thick and thin dashed lines. Modified from Tirone and Ganguly (2010).

5.2 Individual Thermobarometry, Average P-T method and Pseudosections

5.2.1 Individual thermobarometry

Both individual thermobarometry (ITB) and the “average P-T method” (APT), the latter developed by Berman (TWQ software package) and Powell and Holland (1994 and THERMOCALC software package), attempt to determine a limited domain in the P-T space within which the P-T trajectories of mineral reactions within an observed mineralogical assemblage that equilibrated to a unique P-T condition should intersect. Ideally all calculated equilibria for an assemblage in which the minerals are in mutual equilibrium should intersect at a point, which is, however, never the case if there are multiple equilibria, even when the condition of equilibrium is satisfied. This is because of uncertainties in the calculation of the equilibrium P-T trajectories of reactions stemming primarily from those of the available experimental data and thermodynamic properties of the minerals. Because of this problem, it is always desirable to use as many **well calibrated** equilibria as possible rather than a large set of equilibria with variable quality of calibrations.



In the ITB approach, one typically uses a few equilibria in the volatile free systems among which at least two have large difference in their P-T slopes. Often these consist of one exchange equilibrium (or continuous reaction, *e.g.*, Fe-Mg exchange equilibrium between garnet and biotite) and one discontinuous reaction (*e.g.*, $\text{Grt} = \text{Plag} + \text{Al}_2\text{SiO}_5 + \text{Qtz}$: GASP) since these satisfy the desired contrast in their P-T slopes for reasons discussed in the Section 2.3.1. Figure 5.1 is an example of such ITB approach (Ganguly *et al.*, 2000) in which the peak P-T condition was determined from the intersection of GASP and Grt-Bt exchange equilibria calculated from mineral compositions within the scale of a thin section that were inferred to have developed by equilibration at the peak P-T condition; allowing for uncertainties, the P-T trajectory defined by the observed $K_D(\text{Fe-Mg})$ in Grt-Bt defines a narrow band with very steep slope. (The intersection defined by the Grt-Bt thermometric formulation of Holdaway (2000) falls within the kyanite field whereas that defined by the Ganguly *et al.* (1996) Grt-Bt formulation just permits the appearance of sillimanite according to the P-T location of kyanite-sillimanite equilibrium due to Holdaway (1971). The result from the Ganguly *et al.* (1996) formulation was accepted since the rock contains sillimanite.)

Sometimes one finds assemblages that permit use of two discontinuous reactions with substantially different P-T slopes such as the ones illustrated in Figure 5.1. An additional and interesting example applicable to metabasic granulites is the reaction $\text{Pyr} + \text{Grs} + \text{Qtz} = \text{En} + \text{An}$ (acronym: PYGOP), and its iron counterpart $\text{Alm} + \text{Grs} + \text{Qtz} = \text{Fsl} + \text{An}$ (ALGOP) in the assemblage of Grt, Opx, Plag, Qtz (*e.g.*, Perkins and Chipera, 1985). Here two equilibria with substantially different P-T slopes can be calculated using mineral compositions in each Grt-Opx-Plag assemblage within a thin section, such as illustrated in Figure 5.4, using the experimental data for the Mg and Fe end member reactions and accounting for the solid solution effects. The data used to calculate Figure 5.4 are taken from Coolen (1980) who reported many sets of mineral compositions, as determined by microprobe analysis in multiple thin sections, from the Furua Complex, Tanzania. Ignoring the outliers, the cluster of intersections illustrated in Figure 5.4 define a narrow range of peak P-T condition of $9.5(\pm 0.5)$ kb and $790(\pm 30)$ °C. (This figure has been extracted from the power point lecture materials on Thermobarometry for my undergraduate petrology class at the University of Arizona in which there is a question for the students “*Why are the slopes so different?*”. Sometimes I got the correct thermodynamic answer.)

In the ITB method, one relies or should rely on well tested experimental data on equilibria in relatively simple systems, thermodynamic corrections for the effect of additional components and **judicious choice** of phase compositions within a natural assemblage of interest that could be expected to be in equilibrium at the peak or retrograde conditions, depending on the purpose. This approach should yield a reliable P-T estimate if the experimental data in the simple systems and thermodynamic mixing property data of mineral phases are robust. In the current state, experimental data of a limited number of continuous and discontinuous reactions and the mixing property data of the minerals involved in these



reactions seem to be good enough to warrant the use of ITB method based on those equilibria. As examples of the proper application of the ITB method, one may consult Ganguly *et al.* (2000) and Dasgupta *et al.* (2004, 2009).

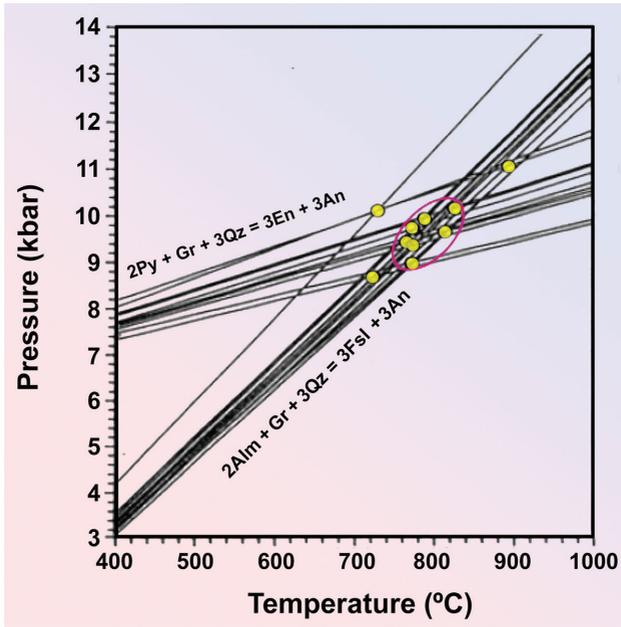


Figure 5.4 P-T condition of metamorphism of granulite facies rocks from the Furua Complex, Tanzania, defined by the calculated positions of two reactions written in terms of Fe and Mg end members in the assemblage Grt-Plag-Opx-Qtz and calculating their displacements due to solid solution effects using compositional data for many samples; each set of data were collected by Coolen (1980) from a single thin section using an electron microprobe. The intersection of the two reactions in each sample is marked by a yellow circle. Neglecting three outliers, these intersections (red ellipse) define a peak P-T condition of 9.5(±0.5) kb and 790(±30) °C.

To my knowledge, the ITB approach for constraining P-T conditions of natural samples was first used by Wood (1975b) to determine the condition of granulite facies metamorphism in the igneous complex of South Harris, Scotland. The rocks consist of Grt-Cpx-Plag in olivine normative and two pyroxene (ortho and clino)-Plag-Qtz in the (garnet absent) quartz normative bulk compositions. Wood (1975b) calculated the P-T relations of the garnet forming reactions in the two compositions ($Ol + Plag \rightarrow Grt$ and $Opx + Plag \rightarrow Grt + Qtz$ – see Fig. 5.4 for the latter) to define the lower and upper pressure limits, respectively, based on the experimental data of the end member reactions and thermodynamic mixing properties of solid solutions. (These calculations relied on the garnet solution



model of Ganguly and Kennedy (1974) – see Section 2.3.3 for the story about the reviewer reaction and publication of this paper.) These were then combined with the P-T relations defined by two geothermometers (two pyroxene and Grt-Cpx), which were still in very preliminary stages of development, to deduce 10-13 kb, 800-860 °C for the condition of granulite facies metamorphism in South Harris. (Using the Grt-Cpx thermometric formulation in Ganguly *et al.* (1996) that incorporates the widely used garnet solution model therein and the associated computer programme – https://www.geo.arizona.edu/~ganguly/pub/P-T_Calc/ – I obtained a temperature of 863-878 °C at 10-13 kb using the compositional data listed for the Grt-Cpx pairs in Wood (1975b)).

5.2.2 Average P-T method and pseudosections

To alleviate the potential problem stemming from reliance on only two to three equilibria that may not be so well constrained, Powell and Holland (1994; THERMOCALC) developed a method of optimisation of the results from the calculation of several possible equilibria in a given assemblage, using the internally consistent thermodynamic data from their THERMOCALC database. The merits and demerits of this approach have been discussed by Dasgupta *et al.* (2004). In principle, it is always desirable to include as many equilibria as possible for the calculation of P-T conditions, but this approach could also lead to problems if:

- (a) the thermodynamic data of all phases, including solid solutions, are not sufficiently well constrained,
- (b) all postulated reactions did not achieve equilibrium simultaneously, and
- (c) the equilibrium P-T conditions of some of the calculated equilibria depend on the activities of fluid species that could not be constrained on the basis of petrographic observations.

In the application of the APT method, dehydration equilibria have sometimes been included assuming $a(\text{H}_2\text{O}) = 1$ (*e.g.*, Stephenson *et al.*, 2000). This assumption, however, cannot be justified, even when there is no mineralogical evidence for the presence of a significant quantity of CO_2 *etc.* in the volatile phase, and for the following reasons.

More than 50 years ago, Miyashiro (1964) pointed out that pelitic rocks often contain graphite and thus the fluid composition in metapelites containing graphite was governed, in the simplest case, by homogeneous equilibrium in the C-O-H system. This was followed by a more detailed study by French (1966) on the abundance of fluid species in the C-O-H system in the presence of graphite, and further elaborated by a number of other petrologists (*e.g.*, Ganguly, 1977; Ohmoto and Kerrick, 1977). The general conclusion was that in a metapelite containing graphite, the $X(\text{H}_2\text{O})$ in the fluid phase was almost never in excess of ~0.75, and often was significantly less. Even when there was no graphite in the protolith and the fluid species were limited to the simplest possible H-O system,



the $X(\text{H}_2\text{O})$ in the vapour phase was significantly less than unity at $f(\text{O}_2)$ in the lower part of the magnetite field because of the high concentration of H_2 (e.g., Sharp *et al.*, 2013; Section 10.5.5.1 in Ganguly, 2020). This is why dehydration equilibria are affected by $f(\text{O}_2)$ conditions even though oxygen is not explicitly involved in such equilibria, as shown in Figure 4.1. This fact was first recognised in the experimental studies on annite stability by Wones and Eugster (1965) and subsequently considered in a number of other studies, experimental and theoretical, on the dehydration equilibria of key metapelitic minerals (e.g., Ganguly, 1968, 1969, 1972; Ganguly and Newton, 1969; Ohmoto and Kerrick, 1977). Thus, a better “average P-T method” approach would be to calculate the optimal P-T condition on the basis of only well constrained **anhydrous** equilibria or adequate prior knowledge of $a(\text{H}_2\text{O})$ if dehydration equilibria are included that, in fact, would require the use of ITB method, as discussed below.

Dasgupta *et al.* (2004) tested the APT method for some assemblages in the Sikkim Himalayas which constitute a part of the well known inverted metamorphic sequence. In an assemblage in which chloritoid was found only as small inclusions in garnet, the optimal P-T condition was calculated from the APT method by including all major hydrous and anhydrous phases except chloritoid, which was obviously out of equilibrium with the matrix phases, and assuming $a(\text{H}_2\text{O}) = 1$. The presence of chloritoid inclusions provides a stringent “external” constraint on the P-T condition of the assemblage in that it must lie below the absolute thermal stability limit of chloritoid defined by the reaction $\text{Chd} = \text{Alm} + \text{Cor} + \text{H}_2\text{O}$ (Ganguly, 1969). Assuming $a(\text{H}_2\text{O}) = 1$, the APT method of Powell and Holland (1994; THERMOCALC) was found to yield a tightly constrained solution of $6.5(\pm 0.7)$ kbar and $605(\pm 11)$ °C. However, the calculated temperature is ~ 20 °C greater than that defined by the absolute stability limit of chloritoid. Use of anhydrous equilibria, on the other hand, yielded P-T condition of $5.9(\pm 1.4)$ kbar, $601(\pm 88)$ °C, which satisfy, within the stated error limits, the constraint imposed by the condition of chloritoid stability, but is associated with too large a temperature uncertainty to be useful for petrological purposes. In comparison, the simultaneous solution of Grt-Bt Fe-Mg exchange and GASP equilibria using the computer programmes of Ganguly *et al.* (1996) (see above for the link) that incorporated their garnet mixing model yielded 5.7 kbar, 550 °C that is lower than the absolute thermal stability of chloritoid by 25 °C. The failure of the average P-T method to yield an acceptable P-T estimate within geologically useful error limits, when restricted to anhydrous equilibria, most likely stems from the thermodynamic mixing property data in the THERMOCALC database. Other violations of phase equilibrium constraints by the results of APT method have been documented and discussed by Dasgupta *et al.* (2004).

In a later study, Dasgupta *et al.* (2009) determined the peak P-T condition of suites of samples from the Lesser Himalayan Crystalline (LHC) schist of the Daling group, Sikkim, using both APT and ITB methods. The former includes both Berman (1990) and Powell and Holland (1994) formulations while the latter was based on GASP plus Grt-Bt formulations of Ganguly *et al.* (1996) and the associated software package referred to above. Instead of setting $a(\text{H}_2\text{O}) = 1$, as



has often been done and incorrectly so, in the typical calculations using the APT method, Dasgupta *et al.* (2009) first determined the peak P-T condition of a sample containing hydrous minerals using ITB. They then calculated $a(\text{H}_2\text{O})$ according to Ganguly and Saxena (1987, their equation 4.48) from the difference between the inferred temperature of the assemblage and the equilibrium temperatures of two “texturally corroborated” dehydration equilibria with $a(\text{H}_2\text{O}) = 1$. This exercise led to $a(\text{H}_2\text{O}) = 0.85\text{--}0.89$ to achieve the observed depression of the dehydration temperatures.

The results of Dasgupta *et al.* (2009) are illustrated in Figure 5.5. It is found that going up section from the garnet isograd, there are both pressure and temperature maxima in the profiles calculated from APT versions of Berman (1990) and Holland and Powell (1994). Dasgupta *et al.* (2009) made the critical observation that the up section sample above the coincident P and T maxima had greater degree of diffusive homogenisation of garnet compared to that in garnet of very similar size at the calculated thermal maximum. This implies, as argued by the authors, that the up section sample experienced higher temperature than the one at the calculated maximum. Secondly, no such P-T maxima was observed for P-T profiles along transects above the garnet isograd in northern Sikkim that are poorer in Mn than those in the Eastern Sikkim. Dasgupta *et al.* (2009), thus, argued that the P-T maxima are artefacts of the inferior quality of the garnet solution model in Berman (1990; TWQ) and Holland and Powell (1994; THERMOCALC). It seems quite possible that the pressure maximum observed by Stephenson (2000) and Catlos *et al.* (2001) along transects of HHC rocks are also artefacts of the method of thermobarometric calculations.

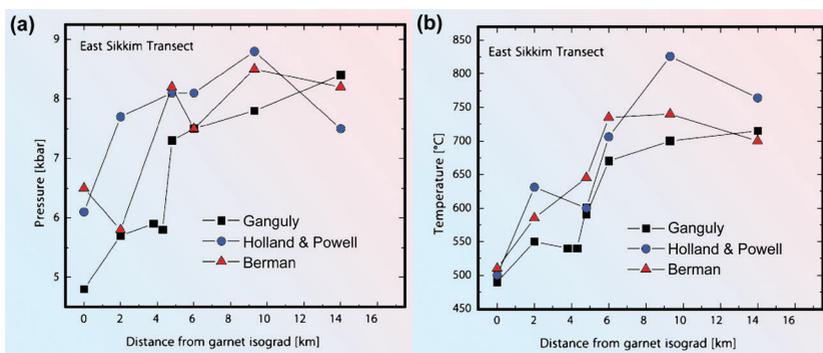


Figure 5.5

Peak P-T conditions of rocks in the Lesser Himalayan Crystalline (LHC) schists, East Sikkim, along a transect from the garnet isograd according to three methods: individual thermobarometry (ITB) according to the formulations of Ganguly *et al.* (1996) and average P-T methods (APT) of Berman (1990) and formulation of Holland and Powell (1994). Modified from Dasgupta *et al.* (2009).



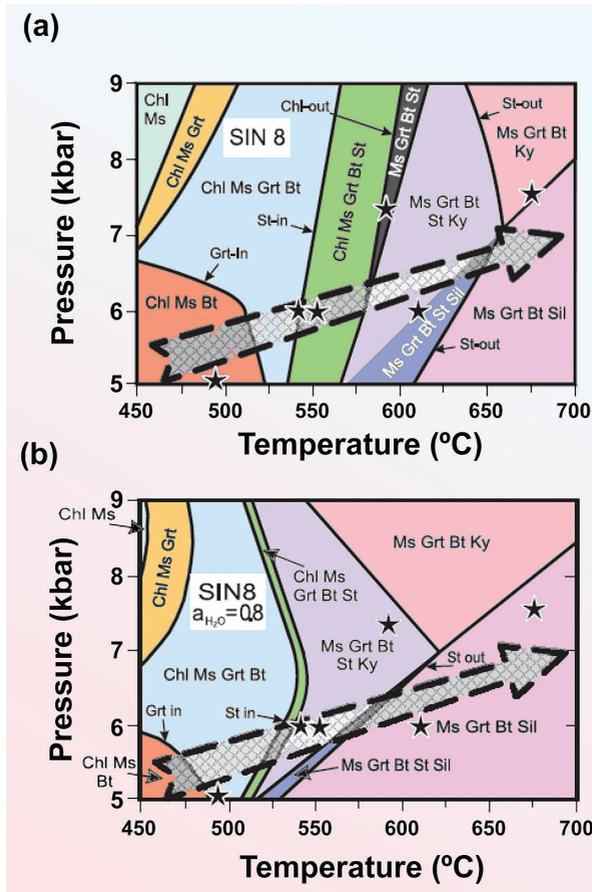


Figure 5.6

Pseudosection calculation using THERMOCALC for the metapelitic bulk composition of the LHC schist in Sikkim, eastern Himalaya. The panels (a) and (b) show the results of calculations using $a(\text{H}_2\text{O}) = 1$ and $a(\text{H}_2\text{O}) = 0.8$, respectively, with the reduced $a(\text{H}_2\text{O})$ value being deduced from the P-T results of ITB (Ganguly *et al.*, 1996) and texturally corroborated dehydration equilibria (see text). The stars indicate the P-T conditions according to ITB method in Figure 5.4. There is better agreement between the observed and calculated phase assemblages (see Dasgupta *et al.*, 2009 for the details) for $a(\text{H}_2\text{O}) = 0.8$. The broad hatched areas with arrows indicate the average of metamorphic field gradient deduced from ITB. Modified from Dasgupta *et al.* (2009).

An example of a pseudosection calculation is given in Figure 5.6, which is reproduced from Dasgupta *et al.* (2009). There are two types of calculations that differ in the input values of $a(\text{H}_2\text{O})$. In the panel (a), $a(\text{H}_2\text{O}) = 1$ whereas in (b), it is 0.8. The P-T conditions calculated from ITB of Ganguly *et al.* (1996)



have been illustrated by stars. The observed mineralogical assemblages of the samples for which the P-T conditions were calculated are found to be compatible with the mineral assemblage fields depicted by the pseudosection in Figure 5.6b. The $a(\text{H}_2\text{O})$ used for this calculation is similar to that deduced independently, as discussed above. This study underscores the importance of using an independent estimate of $a(\text{H}_2\text{O})$ for pseudosection calculations instead of assuming $a(\text{H}_2\text{O}) = 1$, and the best way to do that is to use the P-T results from reliable ITB formulations in conjunction with the conditions of appropriate dehydration equilibria at $a(\text{H}_2\text{O}) = 1$ to calculate the dilution of H_2O in the vapour phase during metamorphism. For further discussion of the methodological details for calculating activities of fluid species, the interested reader may consult Ganguly and Saxena (1987).

5.2.3 Some general observations and comments

The works of Dasgupta *et al.* (2004, 2009) serve to underscore the pitfall of a “black box” approach to thermobarometric calculations, which seems to be a common practice, and also the importance of tracking the extent of diffusive relaxation of compositional zoning in garnet (or in any other mineral) as markers of the change of thermal conditions experienced by a suite of natural samples. Moving too quickly to develop tectonic and geodynamic models to explain anomalous features in P-T profiles may eventually prove to be counterproductive. Additionally, the study of Dasgupta *et al.* (2009) serves to illustrate the point that averaging results obtained from available thermobarometric formulations is a poor practice, and so is any decision in favour of the majority in scientific analysis.

Since pseudosection calculations are based on the principles of equilibrium thermodynamics, the fundamental condition that needs to be satisfied is that equilibrium was achieved within certain spatial domains of a rock sample to which such calculations are applied. A complication arises when mineral compositions are inhomogeneous within a grain scale, since a compositionally zoned mineral was obviously out of equilibrium to a unique set of P-T conditions. A common problem is posed by garnets that had preserved growth zoning at the low-middle grade metamorphic rocks and show evidence of progressive diffusive relaxation of the zoning beginning at the medium grade. Almost complete homogenisation of growth zoning is expected to have been achieved in mm size garnets at $T > 700$ °C or so (Chakraborty and Ganguly, 1991; Dasgupta *et al.*, 2004). However, in the retrograde path the garnets often develop retrograde zoning (Fig. 2.9). The process of diffusive modification of growth zoning and development of diffusion induced retrograde zoning in garnets in metapelites may be appreciated by following the numerical simulations presented by Chakraborty and Ganguly (1991: see their Fig. 15).

When a mineral composition is found to be variable within a single grain, one is confronted with the task of sorting out the composition within a zoning profile that was in equilibrium with other minerals in a particular spatial domain of a sample in order to be able to retrieve temperatures along the prograde and



retrograde paths. Dasgupta *et al.* (2004) addressed the problem with zoned garnet for a suite of samples from the Sikkim Himalayas that may serve as a starting point for working with other metapelitic assemblages (also see Dasgupta *et al.*, 2009). It is, however, completely erroneous to average compositions of the zoned minerals for the purpose of comparison with pseudosection calculations or, for that matter, any type of thermobarometric calculations.

Pseudosection calculation also involves determination of the bulk composition of an **equilibrating** volume of a sample. This step may be problematic. However, when reactions could be inferred from petrographic observations, it is more straightforward to write out the stoichiometrically balanced reactions and calculate the displacements of those reactions with respect to reliable laboratory calibrations, using the compositions of the minerals that seem to constitute equilibrium combinations. Reconstruction of P-T paths using such approach has been illustrated in Figures 5.1, 5.4.

5.3 Mantle Xenoliths and Thermal State of the Upper Mantle

In his 1973 Presidential Address to the Geochemical Society, Joe Boyd presented what he called “a pyroxene geotherm” in which he calculated the P-T conditions of equilibration of mantle xenoliths (Grt-lherzolites) in the Lesotho kimberlites based on the experimental data on the diopside-enstatite “solvus”¹⁸ and MacGregor’s data for the alumina isopleths in the garnet field in the MAS system (Fig. 3.6; the 1974 paper was in press, but MacGregor made it available to Boyd). Boyd’s was a pioneering paper in that it was the first study that tried to constrain the geotherm of the upper mantle in a specific region and geologic time (in this case, Cretaceous, which was the eruption time of the kimberlites that contained the xenoliths) based on thermobarometric study of mantle derived samples and thus opened a new and important field of study. Our only clue to the mantle thermal condition at that time was Clark and Ringwood’s average steady state shield geotherm (Clark and Ringwood, 1964) that was calculated on the basis of heat flow data and heat conduction equation incorporating the effect of radiogenic heat production.

Boyd (1973) found that the xenoliths in his study had two types of textures, sheared and granular, and that their calculated P-T arrays defined two clearly separated regimes with a distinct kink in between; the one defined by the granular group follows the form of the Clark and Ringwood steady state shield geotherm whereas that defined by the sheared group has a steeper T-P slope and lies at higher pressures (Fig. 5.7). Boyd (1973) suggested that the plate movements during the break up of Gondwanaland caused shearing of the nodules and shear

18. Although it is called a solvus, it is better to characterise it as a compositional gap since from a thermodynamic standpoint a solvus forms as a result of instability within a convex upward region of a *continuous* free energy composition relation (the two stable phases have the same structure).



heating above the steady state geotherm. Lane and Ganguly (1980) recalculated the P-T conditions of the same suite of xenoliths using Boyd's microprobe data, but using their version of the alumina isopleths (Fig. 3.6b) plus the Grt-Cpx Fe-Mg exchange geothermometer of Ganguly (1969). The results, which are illustrated in Figure 5.7, differed somewhat from those of Boyd (1973) and notably with respect to the presence of a "kink" – none was necessary in the L-G calculations – but still the P-T arrays of the granular and sheared xenoliths were clearly separated. With respect to the presence of kink in the "xenolith geotherm", it should be easy to see, as pointed out by Howells and O'Hara (1978), that treatment of the alumina isopleths as linear P-T arrays while they actually have curvatures that are convex towards the temperature axis would impart an opposite curvature to the arrays, giving the appearing of a "kink" (the curvature of the isopleths stem from the nature of variation of the C_p and thermophysical properties as function of T and/or P).

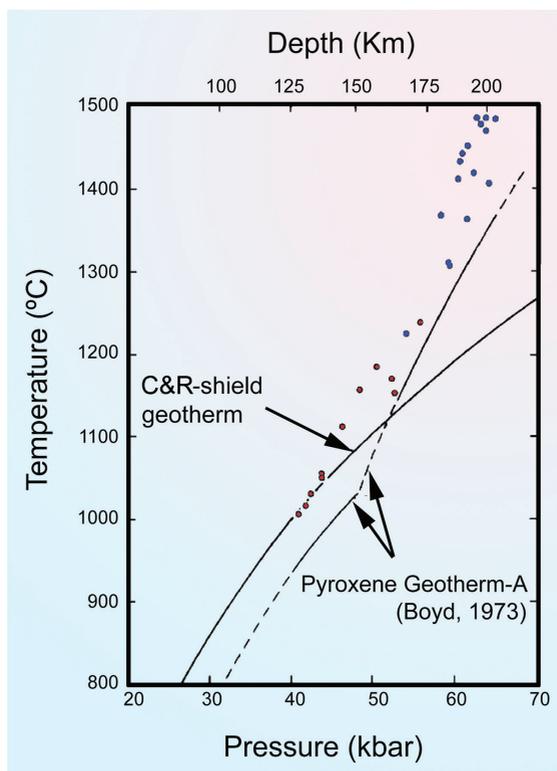


Figure 5.7

Calculated P-T conditions of garnet-lherzolite nodules in the kimberlite pipes from Lesotho, S. Africa. The symbols represent calculations by Lane and Ganguly (1980), based on raw Al_2O_3 content of enstatite (Fig. 3.6b) and



Grt-Cpx Fe-Mg exchange thermometer by Ganguly (1979), using the mineral compositional data from Boyd (1973). The red and blue circles indicate, respectively, the granular and sheared nodules. Modified from Lane and Ganguly (1980).

On my first sabbatical leave in 1981 I went to India, making it a combination of a family visit and professional work, and spent part of my time collecting xenolith samples from the drill cores of the Geological Survey of India in the Warzakarur kimberlite pipes in the southern part of India. The extremely difficult technical and often insurmountable bureaucratic logistics of this type of endeavour were manoeuvred and short circuited by my younger brother, Surya Gangopadhyay, who was a geologist with the survey and was posted in its Hyderabad branch that oversaw the Warzakarur operation. I returned to USA with a precious collection of garnet-lherzolite and some eclogite xenoliths but was unable to begin any research with them for a shortage of manpower and support. The opportunity finally came through a UNESCO programme that arranged for Indian scientists to spend a year abroad to carry out collaborative research with scientists in the western world and thus gain firsthand experience with the new frontiers of research and teaching outside of their traditional comfort zones. I was lucky enough to have my classmate in India, Prasanta Bhattacharya, visit me through this programme and the Warzakarur xenoliths turned out to be an ideal problem for him to work on.

We carried out detailed petrological and associated thermobarometric studies of these xenoliths and explored the geophysical implications of the results (Ganguly and Bhattacharya, 1987). The P-T conditions of the Grt-lherzolites were calculated using both Grt-Opx (yet to be published; Lee and Ganguly, 1988) and Grt-Cpx (Ganguly, 1979) Fe-Mg exchange thermometers along with the alumina isopleth data in enstatite in equilibrium with garnet from Lane and Ganguly (1980). It was found that the P-T arrays defined by the Proterozoic mantle xenoliths from Warzakarur and Cretaceous mantle xenoliths from Lesotho (Lane and Ganguly, 1980; Fig. 5.7) are quite similar (Ganguly and Bhattacharya, 1987). Palaeogeographic reconstruction shows that India and Africa were adjacent landmasses until their breakup during the Gondwana period. Thus, as argued by Ganguly and Bhattacharya (1987), the similarity of thermal profiles defined by the two sets of xenoliths suggests that the upper mantle geotherm in the continental shield area was in a near steady state condition from the Proterozoic to the Cretaceous that marked the eruption periods of the Warzakarur and Lesotho xenoliths, respectively.

5.4 Thermal Perturbation During Granulite Facies Metamorphism

Following a gap of several years, we returned to the thermobarometric data of the mantle xenoliths in the Indian shield in connection with our study of the problem of charnockitisation and granulite facies metamorphism of which the



southern India is a classic locality (charnockites are orthopyroxene-bearing rocks of broadly granitic chemistry). In this study (Ganguly *et al.*, 1995), we calculated the Proterozoic geotherm in the Indian shield using the steady state solution of the heat transfer equation that yields

$$T(Z_2) = T(Z_1) + \frac{q_m}{K_z} (Z_2 - Z_1) - \frac{H_s D^2}{K_z} \left(e^{-Z_2/D} - e^{-Z_1/D} \right) \quad (5.1)$$

where $T(Z_i)$ is the temperature at the depth Z_i , D is a scaling depth (related to a model of exponential decrease of heat production rate with depth), q_m is the mantle heat flux at $Z \gg D$, H_s is the volumetric heat production rate of the surface rock and K_z is the mean thermal conductivity between the depths Z_2 and Z_1 . The steady state T vs. Z relation was calculated using a finite difference scheme. Of the various parameters in this equation, q_m was most poorly constrained. The standard practice for the determination of q_m was to make use of the Birch-Lachenbruch relation, that is the observed linear relation of the surface heat flux, q_s , vs. H_s , with the intercept at $H_s = 0$ being equated to q_m and the scaling depth (D) to the slope of the line (*e.g.*, Turcotte and Schubert, 1982). Deviating from this practice, and especially since the heat flow data in the southern Indian shield was scanty, we calculated a T vs. Z relation, treating q_m as a floating variable, such that the calculated thermal profile matches the xenolith P-T data. The resulting steady state Proterozoic geotherm (~1 Ga) in the Indian shield, which corresponds to $q_m = 21.3 \text{ mW/m}^2$, is illustrated in Figure 5.8a, in which the P-T data of the Warzakarur mantle xenoliths from the South Indian shield area are illustrated by crosses. The 2.5 Ga Archean geotherm was calculated from the Proterozoic geotherm using a model of Turcotte and Schubert (1982) on the cooling of a convecting upper mantle.

Figure 5.8a also shows the thermobarometric data for the Archean charnockites and granulites from the South Indian shield area. It is evident that these rocks had not formed at the steady state geothermal condition. Instead, there must have been a transient thermal perturbation leading to formation of these high temperature rocks. The possible reasons behind this perturbation have been discussed by Ganguly *et al.* (1995) in terms of the quantitative effects of crustal thickening due to overthrusting of the rocks and convective heat flux associated with degassing of CO_2 from a depth of 90-125 km. With respect to the latter, previous workers (Janardhan *et al.*, 1982; Newton, 1988) suggested that the formation of charnockites in the southern Indian shield was associated with copious CO_2 influx from a deep seated source, possibly the mantle. Figure 5.8b shows the transient thermal perturbation due to the CO_2 fluxing with a Darcy velocity ($V\phi$) of 0.3 cm/yr that matches the P-T condition of the charnockites and granulites (here V is the true velocity and ϕ is the porosity of the medium). Ganguly *et al.* (1995) offered a combination of overthrusting and CO_2 fluxing as a plausible explanation of the thermal perturbation leading to the formation of the charnockites and granulite facies rocks in Southern India; irreversible adiabatic decompression of the fluid might also have contributed to the heating (Ganguly, 2005).



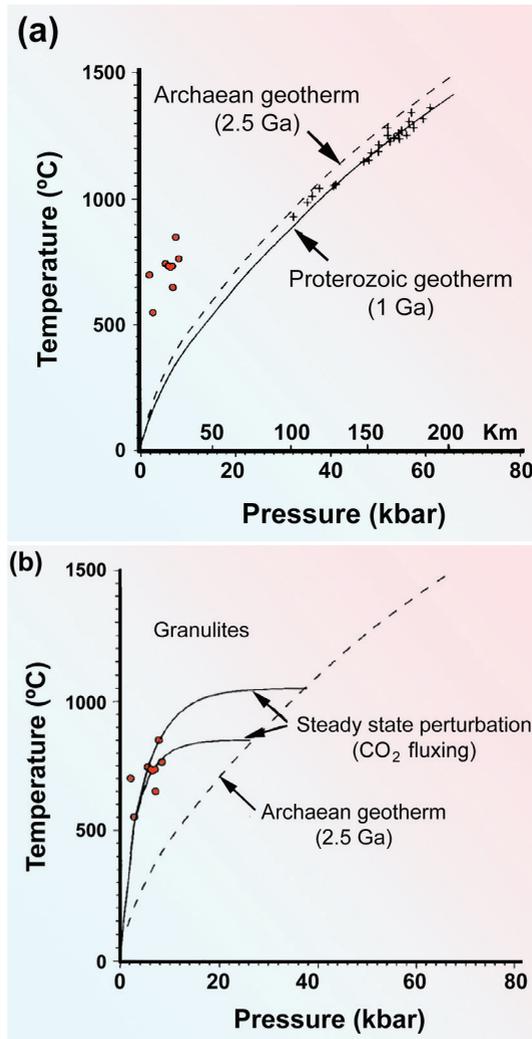


Figure 5.8

(a) Steady state lithospheric geotherm in the south Indian shield at c. 1 Ga (solid line) and c. 2.5 Ga (dashed line). The 1 Ga Proterozoic geotherm was calculated on the basis of P-T data (crosses) of mantle xenoliths in the Warzakarur kimberlite pipes and heat flow plus volumetric heat production rate data of the surface rocks. The 2.5 Ga steady state Archean geotherm was calculated from the 1 Ga geotherm using a cooling model of convecting mantle, according to Turcotte and Schubert (1982). The filled red circles show the P-T data of the charnockites/granulites in the south Indian shield, collected from the literature. (b) The calculated transient thermal perturbation due to degassing of CO₂ from depths of 90-125 km within the mantle with a Darcy velocity of 0.3 cm/yr. Modified from Ganguly *et al.* (1995).



Dapine *et al.* (2008) considered crustal melting and melt focusing as a plausible reason for thermal perturbation of steady state geotherms to generate transient thermal profiles in the lower-mid crustal level for granulite facies metamorphism. They used the same heat transport equation as Ganguly *et al.* (1995) but with an additional term to account for the effect of latent heat of melting. The thermal profiles calculated by Dapine *et al.* (2008) are similar in form, including an initial isothermal segment, to those illustrated in Figure 5.8b for CO₂ fluxing mediated thermal perturbation.

Newton (2020) recently proposed a plate tectonic scenario in which a generation of CO₂ and halogen-rich asthenospheric melts was envisioned to have invaded the continental margins. The melt was supposed to have provided the heat source for the attainment of the granulite facies temperatures whereas the liberated volatiles were to have caused depression of the H₂O activity, thereby preventing melting of the mid-crustal rocks. Newton (2020) did not consider the additional heating effect stemming from the transport of the degassed CO₂. Within the framework of the scenario proposed by Newton (2020), it seems possible that the thermal perturbation needed for granulite facies metamorphism was a consequence of the cumulative effect of melt fluxing and CO₂ degassing from the melt, with the latter playing the additional role of protecting the rock from melting.



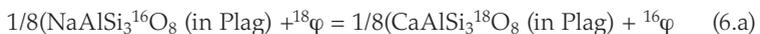
Since the seminal work of Urey (1947) that I have discussed above and an immediate follow up study by Biegeleisen and Mayer (1947) on the statistical thermodynamic aspects of stable isotope fractionation, the field of stable isotope geochemistry has remained a very active field, as evidenced by the publications of three volumes, separated by a period of more than thirty years, in *Reviews in Mineralogy and Geochemistry* (RiMG) series (Valley *et al.*, 1986; Valley and Cole, 2001; Teng *et al.*, 2017) along with a large volume of research and review papers. These works primarily deal with experimental determination and statistical thermodynamic aspects of stable isotope fractionation, and in recent years with application of density functional theory (DFT) to the problem. In this section, I discuss some thermodynamic aspects and DFT based advancements with which I had direct involvement.

6.1 Intrusion of Classical Thermodynamics

Classical thermodynamics has found very little application in the field of stable isotope fractionation since isotopes of an element mix effectively ideally so that the equilibrium constant (K) of an isotopic exchange reaction is given simply by the ratio of the isotopic ratios (α) in the two compounds. Thus, for example, $K = \alpha = (^{18}\text{O}/^{16}\text{O})_{\text{A}} / (^{18}\text{O}/^{16}\text{O})_{\text{B}}$ for the exchange reaction $^{16}\text{O-A} + ^{18}\text{O-B} = ^{18}\text{O-A} + ^{16}\text{O-B}$. However, the K for oxygen isotope exchange between plagioclase and quartz was found to depend on the anorthite content of the plagioclase. There did not seem to be any satisfactory explanation for this compositional dependence of the fractionation factor. Here my familiarity with solution thermodynamics came in handy. When the problem came to my attention, I immediately recognised that this dependence of $\alpha(\text{Plag-Qtz})$ on the anorthite content of plagioclase is a consequence of the reciprocal solution effect that has been discussed in Section 2.3.3, and a linear relation analogous to equation (2.15) should hold between $\ln\alpha(\text{Pl-Qtz})$ and X_{An} . With this insight, I derived the following relation between $\ln K(\text{Plag-}\varphi)$ and X_{An} , where φ is a stoichiometric phase, making use of the fact that the isotopes of oxygen mix ideally in the oxygen sites of the phases, but the activity coefficients of the isotopes are not unity because of the effect of the changing composition in the Ca-site (Ganguly, 1982b).

$$\ln K(\text{Pl-}\varphi) = \ln K_{(a)} - X_{\text{An}} \ln K_{(b)} \quad (6.1a)$$

where $K(\text{Plag-}\varphi)$ stands for the ratio of $^{18}\text{O}/^{16}\text{O}$ in plagioclase to that in the phase φ at equilibrium, $K_{(a)}$ is the equilibrium constant of the isotopic exchange reaction written in terms of one mole of the exchangeable species



and $K_{(b)}$ is the equilibrium constant of the reciprocal reaction



With some manipulations, the above relationship reduces to

$$\ln K(\text{Plag}-\varphi) = \ln K(\text{Ab}-\varphi) - X_{\text{An}} (\ln K(\text{Ab}-\varphi) - \ln K(\text{An}-\varphi)) \quad (6.1b)$$

where $K(\text{Ab}-\varphi)$ stands for the equilibrium constant of the conventional isotopic exchange reaction between pure end member albite (Ab) and φ , viz. $1/8(\text{NaAlSi}_3^{16}\text{O}_8) + {}^{18}\varphi = 1/8(\text{NaAlSi}_3^{18}\text{O}_8) + {}^{16}\varphi$, and similarly for $K(\text{An}-\varphi)$. This, indeed, is the relation assumed by O'Neil and Taylor (1967) and Matsuhisa *et al.* (1979) to fit the experimental data for oxygen isotope fractionation between plagioclase and a stoichiometric phase as a function of the anorthite content of plagioclase.

My paper initially got a very unfavourable review by a highly distinguished geochemist who made major contributions in the field of stable isotope geochemistry. However, thanks to the chance given to me to respond to the reviewer's comments by Karl Turekian, who was responsible for the editorial handling of the paper for EPSL and once again came to my rescue (see Section 3.2), the paper finally made its way into an EPSL volume (Ganguly, 1982b). The reviewer was so embarrassed to find out where he went wrong that he immediately sent telegrams to both Turekian and myself, admitting his error and recommending publication of the paper. Unfortunately, however, the paper received very little attention in the field of oxygen isotope thermometry, but recently I found out that Tom Chacko has unpublished experimental data on oxygen isotope fractionation between plagioclase and calcite from his days at Chicago that conform to the behaviour predicted in the EPSL paper (equation (6.1)); hopefully, he will publish the data one of these days. Tom was unaware of my paper.

I met the reviewer of my EPSL (1983) paper in the Goldschmidt Conference in 1999 in Tucson, Arizona. We had not met before and when someone introduced me to the reviewer during an evening of unstructured social activity, the first thing that he mentioned was his review of my EPSL paper! I hasten to add at this point that the reviewer of my paper did not suffer from a lack of knowledge of thermodynamics but from carelessness and perhaps overconfidence. We return to one more application of classical thermodynamics to the field of stable isotope fractionation in the Section 6.2.1.

Let me end this section with a quote from an e-mail to me by Zach Sharp, one of the leading scientists in the field of stable isotope geochemistry (Zach did his Ph.D. under the late Eric Essene, a foremost figure in petrology in our generation and whom I personally miss greatly): *"The great thing I learned from Eric was thermodynamics. Even if you don't understand the gory details, a good conceptualization of thermo gives us a leg up on the rest of the world."*



6.2 Recent Advancements Using Density Functional Theory

In his Nobel Lecture for winning the 1998 prize in Chemistry for the “development of density functional theory”, Walter Kohn made the following remark (Kohn, 1999):

“There is an oral tradition that, shortly after Schroedinger’s equation for the electronic wave-function ψ had been put forward and spectacularly validated for simple small systems like He and H₂, P.M. Dirac declared that chemistry had come to an end – its content was entirely contained in that powerful equation. Too bad, he is said to have added, that in almost all cases, this equation was far too complex to allow solution.”

Although built on the Schrödinger equation, DFT bypasses its direct solution for many electron problems, which is impossible, even with the aid of the fastest computers, for many practical problems and especially for those of geological interest. DFT based computational protocols have been implemented in several commercial software packages such as Gaussian (developed by Pople who shared the Nobel Prize with Kohn), VASP (Vienna *ab initio* software package), CRYSTAL *etc.*, thus making possible the computation of thermodynamic properties of materials, in the framework of statistical thermodynamic formalisms, with sufficiently high level of accuracy for many purposes.

6.2.1 Hydrogen isotopic fractionation between mineral and hydrogen/water systems

There have been numerous studies on the experimental determination of stable isotope fractionations between coexisting phases, using mass spectrometers as the primary analytical tool. Where the main interest has been on the determination of fractionation between two minerals, as in the case of oxygen isotope thermometry such as that based on ¹⁸O/¹⁶O ratios in quartz and magnetite, the experiments had been carried out between water and each of the minerals. A mineral-mineral fractionation was derived from the experimental data for the two mineral-water fractionations. In the latter, the minerals were separated from the experimental products or “charge” that was quenched from an experiment at a desired P-T condition in a hydrothermal apparatus. The isotopic ratios were then measured in the mineral separates and water in a sensitive mass spectrometer. It was recognised much later in the game that the data on the isotopic ratios of mineral and water were sometimes compromised by the dissolution (\pm re-precipitation) of the finely ground mineral grains in water. Subsequently, advancements have been made to circumvent the experimental problem by (a) replacing water with calcite (*e.g.* Clayton *et al.*, 1989), (b) using hydrogen (Venemann and O’Neil, 1996) instead of water, and (c) using a large grain-water combination and analysing the grain by Secondary Ion Mass Spectrometry (SIMS) (Chacko *et al.*, 2001).

Complementing the experimental efforts, several groups (*e.g.*, Schauble *et al.*, 2006; Rustad *et al.*, 2008; Méheut *et al.*, 2010; Huang *et al.*, 2014; Asaduzzaman



and Ganguly, 2018, 2021; Colla and Casey, 2019 *etc.*) have been engaged in recent years in the DFT based calculation of stable isotope fractionation in systems of interest in geochemistry and palaeothermometry. These studies are important for (a) sorting out the conflicting experimental data in a system, and (b) providing constraints for extrapolation of experimental data to lower temperatures that are of interest in palaeothermometry but are much below the kinetically feasible temperatures for attainment of equilibrium within the laboratory time scale.

It has been argued by Asaduzzaman and Ganguly (2018) that the effect of anharmonicity, if any, should substantially cancel out in the expression of equilibrium constant of isotopic exchange reactions in terms of partition functions, at least in the low temperature range of interest in palaeothermometry. Ganguly (2020) showed the excellent agreement (Fig. 6.1) between the equilibrium constants for hydrogen isotopic exchange reaction in the water- hydrogen system calculated separately from the thermochemical data and reduced partition function ratios (RPF). The latter is the ratio between the molecular partition functions of the heavy (*) and light isotopes, q_i/q_i^* , of an element in a compound i expressed in terms of vibrational frequencies making use of the harmonic Teller-Redlich product rule, as discussed in Section 2.2.2.

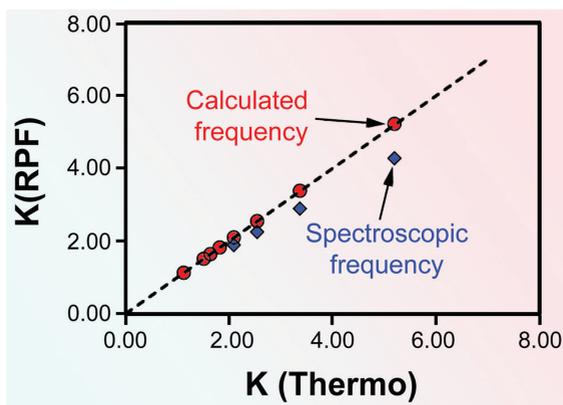


Figure 6.1

Comparison of the equilibrium constant, K , of the isotopic exchange reaction $\text{H}_2\text{O} + \text{D}_2 = \text{D}_2\text{O} + \text{H}_2$ calculated from (harmonic) reduced partition function ratio (RPF) formulation in statistical thermodynamics with the results from thermochemical calculations at 1 bar, 400 – 2000 K. Circles: RPF results using DFT-based vibrational frequencies; diamonds: those using spectroscopic frequencies. The dashed line represents the perfect agreement between the statistical thermodynamic and thermochemical calculations of the equilibrium constant. Modified from Ganguly (2020).

Traditionally, the vibrational modes and frequencies have been derived from spectroscopic data. However, modern advancements in the development of sophisticated computational software packages in quantum chemistry based



on DFT have made it possible to calculate the vibrational properties quite accurately, thus enabling reliable calculation of the equilibrium constants of isotopic exchange reactions. For the data illustrated in Figure 6.1, the K calculated from DFT derived data of vibrational frequencies has performed even better, in terms of agreement with equilibrium constant calculated from thermochemical data, than that derived from the spectroscopic data. Of course, the DFT based calculations are much easier said than done as there is yet no unique recipe for performing the calculations. However, we (Asaduzzaman and Ganguly, 2018, 2021) have developed an approach for calculation of hydrogen isotopic fractionation in mineral-hydrogen/water systems that have performed well in terms of agreement with robust experimental data. Two examples from our work are illustrated in Figures 6.2, 6.3.

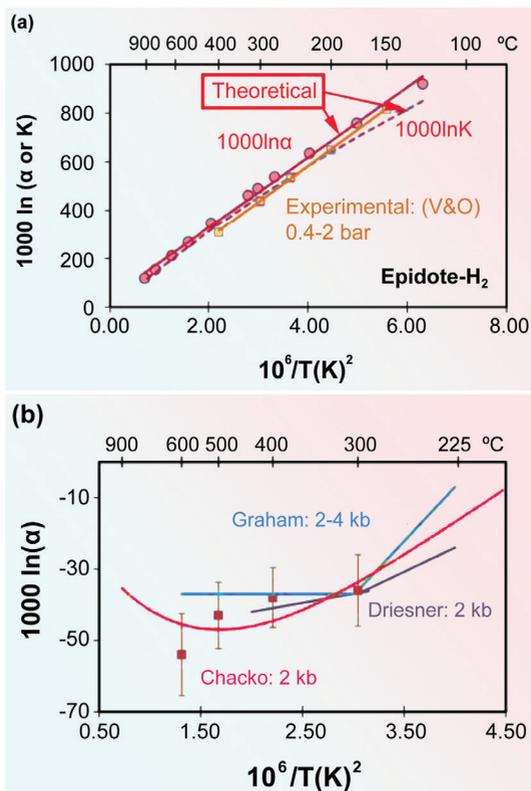


Figure 6.2

Comparison of the calculated (RPFR and DFT-based) $\ln\alpha$ vs. $1/T^2$ relation (a) at 1 bar for D-H fractionation in the epidote-hydrogen system with the experimental data at ~0.4 – 2 bar (Vennemann and O’Neil, 1996); and (b) for epidote-water system with experimental data (2- 4 kb) and data derived by Driesner from those in the panel (a) after correcting for the hydrogen-water



fractionation and pressure effects. The α stands for D/H ratio in the mineral to that in the gas phase. Circles and squares: calculated and experimental data, respectively. In the lines labeled as theoretical in (a), the solid and dashed lines represent the least squares fits to the calculated data for $1000\ln\alpha$ and $1000\ln K$, respectively. In (b), the solid curved line is a theoretical fit to the experimental data of Chacko *et al.* (1999). Modified from Asaduzzaman and Ganguly (2018).

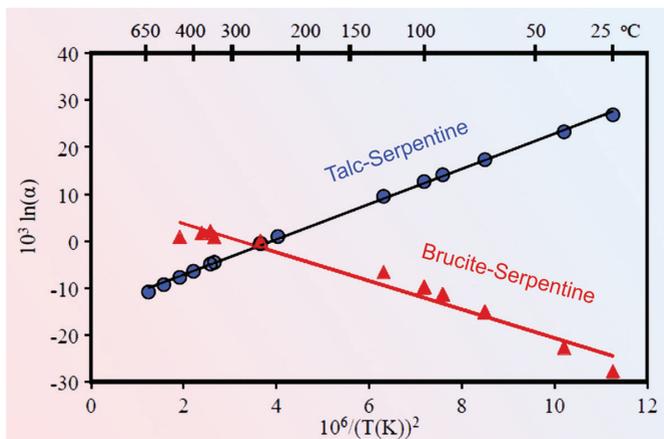
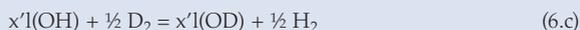


Figure 6.3 Calculated hydrogen isotope fractionation in the talc-serpentine and brucite serpentine pairs vs. $1/T(K)^2$. From Asaduzzaman and Ganguly (2021).

Text Box 6.1 – Conversion of equilibrium constant to fractionation factor

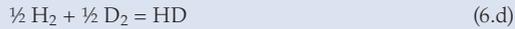
Now back to some classical thermodynamics. There are two calculated curves in Figure 6.2a, labelled $1000\ln\alpha$ and $1000\ln K$. Here α refers to the bulk fractionation factor, *i.e.* the bulk (D/H) ratio in the crystal to that in the hydrogen gas ($\alpha = (D/H)_{x1}/(D/H)_{hyd}$). This is the quantity determined in mass spectrometric analyses of mineral separates and extracted gas after an experiment. However, the parameter that was calculated from statistical thermodynamics is the equilibrium constant of the exchange reaction



The $K_{(c)}$ equals α if there is negligible content of other D and H bearing species in the gas phase. However, in general this is not the case since the content of the mixed isotope species, DH, in the gas phase may not be negligible at all conditions of practical interest in low temperature geochemistry and thermometry. Thus, a correction needs to be made to convert K to α . This is a general problem that needs to be recognised when comparing the results of statistical thermodynamic calculations that yield an equilibrium constant of an isotopic exchange reaction with experimental



data that yield bulk isotopic fractionation. For the specific problem of the hydrogen isotopic fractionation, it has been shown that $\alpha \approx 2K/K_{(d)}$, where $K_{(d)}$ is the equilibrium constant of the homogeneous gas phase reaction



In Figure 6.2a the solid curve labelled $1000\ln\alpha$ was calculated, using the above relation (within the box), from the dashed curve labelled $1000\ln K$ that was derived from statistical thermodynamics using DFT based data for the vibrational frequencies (see also Colla and Casey, 2019). There is excellent agreement between the calculated and experimental data for the hydrogen isotope fractionation factor that are illustrated in this figure.

For systems for which $\ln\alpha < 0$ within the experimental range, linear extrapolation of the $\ln\alpha$ vs. $1/T^2$ relation derived by fitting the experimental data could lead to grossly erroneous results. This is because there must be a minimum in the curve since $\ln\alpha$ would be zero at some high temperature (α tends to unity as T increases). The calculated $\ln K$ vs. $1/T^2$ relation for hydrogen isotopic fractionation between a number of hydrous minerals and water(gas) shows the presence of a minimum, such as the one illustrated in Figure 6.2b, in the temperature range 135-500 °C (Méheut *et al.*, 2010; Asaduzzaman and Ganguly, 2018). For such non-linear behaviour, the form $\ln K = A + B/T + C/T^2$ seems to fit the data well; this form also has a theoretical justification (Criss, 1999).

Where experimental data are insufficient to tightly constrain the A and B parameters, the non-linear extrapolation beyond the experimental range may be carried out with the aid of complementary statistical thermodynamic calculation. An example of this approach is shown in Figure 6.2b. In this figure, the experimental data of Chacko *et al.* (1999) on hydrogen isotopic fractionation between epidote and water at 2 kb, shown by square symbols with error bars, were fitted and extrapolated with the aid of a theoretical curve. The latter was calculated from statistical thermodynamics and DFT based vibrational frequencies but was shifted upwards by 5.5 ‰ to obtain best least squares fit to the experimental data. It predicts well the low temperature data of other workers (Graham *et al.*, 1980; Driesner, 1997) without requiring a discontinuous change of slope. Also, this empirical shift is in accord with the experimentally determined effect of pressure by Horita *et al.* (2002) on the hydrogen isotope fractionation between brucite and water.

We have extended the above approach to calculate the hydrogen isotope fractionation in the talc-serpentine-brucite-water system (Asaduzzaman and Ganguly, 2021). The calculated talc/serpentine-water data have been found to be in excellent agreement with the reliable experimental data. Combining the mineral-water data, we have formulated two palaeothermometers based on hydrogen isotope fractionation between talc/brucite and serpentine. The results are illustrated in Figure 6.3 where $\alpha = (D/H)^A / (D/H)^{\text{serpentine}}$ with $A = \text{talc/brucite}$. For brucite-water, we have used the experimental data spanning a wide range of



temperature and involving data from both reversal and synthesis experiments (see Asaduzzaman and Ganguly, 2021, for the rationale behind this approach). The system of mineral-water and mineral-pair fractionation relations enable simultaneous determination of temperature and source of water in the serpentinisation process (the thermometers are sufficiently sensitive to temperature change below ~250 °C). For example, it was shown (also see Méheut *et al.*, 2010) that the formation of a suite of oceanic serpentines took place by interaction with ocean water, without any significant admixture with the magmatic water.

Since hydrogen diffusion in a mineral is much faster than oxygen diffusion, it is likely that the oxygen isotope thermometry of a mineral pair (*e.g.*, brucite-serpentine) would yield a higher temperature than the hydrogen isotope thermometry for the same pair in slowly cooled rocks. If the hydrogen diffusivity in the minerals is known, then the difference between the two thermometric temperatures could be modelled to obtain the cooling rate if there is a monotonic relation between temperature and time.

6.2.2 Clumped isotopic thermometry

A problem with palaeotemperature studies based on the oxygen isotopic fractionation between a carbonate mineral and ocean water is that the $^{18}\text{O}/^{16}\text{O}$ ratio of the ocean water from which a carbonate mineral precipitated in the ancient past is very difficult to constrain with sufficient accuracy. This problem led to the development of the field of “clumped isotope” thermometry in which one considers a homogeneous equilibrium within a carbonate mineral, such as



where M stands for a divalent cation such as Ca^{2+} and Mg^{2+} . The parenthetical groups are known as isotopologues. The equilibrium constant of this type of homogeneous equilibrium is sensitive to temperature, thus affording a means of palaeothermometry without requiring knowledge of the chemistry of ocean water from which a carbonate mineral had precipitated. This is a developing field that is known as Clumped Isotope Thermometry (Ghosh *et al.*, 2006; Schauble *et al.*, 2006). Although there are other homogeneous exchange equilibria involving different isotopologues, the primary focus in this field has been on the one written above since it involved the most abundant (67 ppm) doubly substituted carbonate ion, $(^{13}\text{C}^{18}\text{O}^{16}\text{O}_2)^{2-}$, which is advantageous for mass spectrometric analysis. Experimental calibration of the temperature dependence of isotopic fractionation within a carbonate mineral requires phosphoric acid digestion of carbonate mineral to release CO_2 and analysis of the latter for the isotopic ratio in a mass spectrometer. It is assumed that there is negligible isotopic fractionation during acid digestion. This assumption may be questionable. A comprehensive discussion of the problem and a remedial measure may be found in Paramanik *et al.* (2020).



From a thermodynamic point of view, the clumped isotope thermometry is analogous to the intra-crystalline exchange or order-disorder thermometry of pyroxene discussed in the Section 2.2.1 (equation (2.5)) and is amenable to first principles calculation that has been discussed above for hydrogen isotope fractionation between two different phases. This step has been taken by Schauble *et al.* (2006). Their results for the equilibrium constant of the above reaction *vs.* $1/T^2$, along with comparison with experimental data (Ghosh *et al.*, 2006), are illustrated in Figure 6.4.

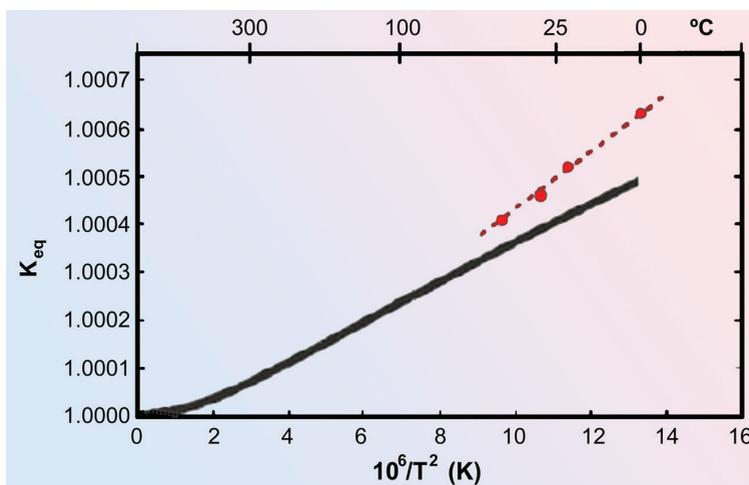


Figure 6.4 Equilibrium constant of the homogeneous clumped isotope exchange reaction (6.e) in calcite as a function of temperature, as calculated from RPFM formulation and DFT based vibrational frequency data. Filled circles illustrate the experimental data of Ghosh *et al.* (2006) involving mass spectrometric determination of the isotopic ratios in calcite. Modified from Schauble *et al.* (2006).

It should also be noted that the kinetics of clumped isotope fractionation may also be treated in the same way as that used for Fe-Mg order-disorder reaction in a mineral (Section 2.4.1; Fig. 2.6a), with appropriate substitutions for the exchangeable units (*i.e.* isotopologues for Fe and Mg in the lattice sites). If there is any demonstrable resetting of the bulk clumped isotopic fractionation during cooling, then this approach may yield quantitative constraints on the cooling rate in the ancient environments.



7. HIGH TEMPERATURE THERMOCHRONOLOGY

7.1 Closure Temperature, Closure Profile and Cooling Rate

As I have mentioned in the Section 1, geochronologists usually determine cooling rates of rocks using a combination of ages of mineral samples separated from the same rock and their corresponding closure temperatures (T_c) that are typically assumed to have fixed values, with some (empirical) uncertainties. An example of this type of work is shown in Figure 7.1. To recapitulate, a closure temperature of a decay system in a mineral is the temperature at which the system becomes effectively closed with respect to diffusion of the species of interest within a mineral grain during cooling. From a physical standpoint, the T_c of a decay system for a mineral, such as that for the Sm-Nd system for garnet, cannot be a unique quantity, but instead should increase with increasing grain size of the mineral and cooling rate. And indeed, these dependencies have been explicitly shown in the expression derived by Martin Dodson in his foundational paper on this subject

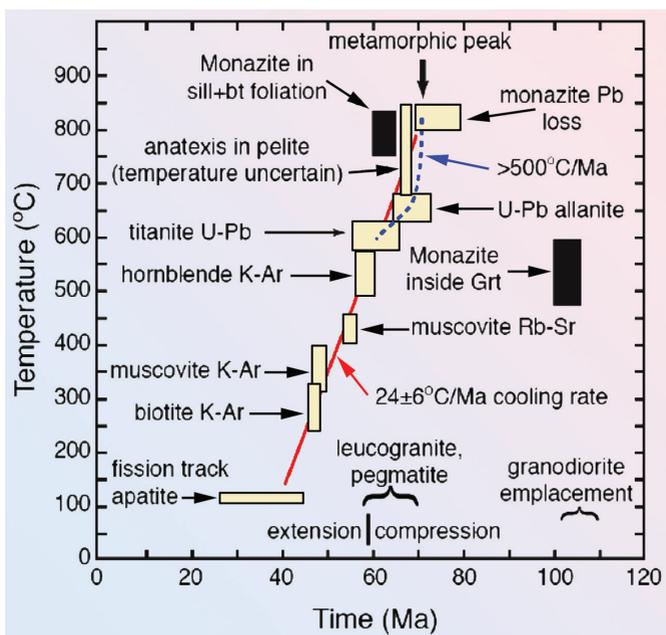


Figure 7.1 Mineral age vs. corresponding conventional closure temperature relation of multiple decay systems from the Valhalla Complex. Modified from Spear and Parrish (1996).



(Dodson, 1973). However, there had been often no specification of grain size or cooling rate in a T_c value specified for a decay system in a mineral in the geochronological or related literature.

The dependence of T_c on cooling rate may be ignored if it is small, but I did not find any paper that tested it for geologically reasonable cooling rates when I started working on the problem of closure temperature. Furthermore, failure to recognise the dependence of T_c of a decay system in a mineral on cooling rate and grain size, especially the latter, led to wide divergence among the empirically derived T_c values for the Sm-Nd decay system in garnet for which the estimates varied from ~400 to 800 °C (Ganguly *et al.*, 1998 and references therein). Additionally, in some studies (*e.g.*, Göpel *et al.*, 1994), the inferred peak metamorphic temperature was found to be lower than the closure temperature of a decay system in a mineral, as calculated from the Dodson formulation or estimated empirically and assumed to be a unique quantity, thus leading to speculation of complex thermal history of the host rock.

It is possible that during a metamorphic episode (M1), a decay system had closed within a mineral at a temperature that is higher than the peak temperature (T_p) of a subsequent episode (M2). If the latter did not attain sufficiently high temperature to induce diffusion of the daughter nuclide in the mineral grains of interest then, of course, the $T_c(M1) > T_p(M2)$. This is, however, a different situation than inferring the existence of an earlier metamorphic episode based on the T_c calculated according to the Dodson (1973) formulation (or estimated empirically) exceeding the T_{peak} of a known metamorphic episode. Here the problem may simply be a consequence of an erroneous application of the Dodson (1973) formulation beyond its domain of validity, as discussed below.

In his 1973 paper, Dodson gave the expression for closure temperature as a function of cooling rate, activation energy of diffusion and grain size in the Abstract of the paper making it easy, perhaps unduly so, for use by the geochronological community without paying attention to the assumptions made in the derivation of the equation. I was struck by the fact that the formulation is independent of the peak temperature experienced by the system. From my early work (Ganguly, 1982b) with the numerical simulation of the evolution of Fe-Mg ordering state in orthopyroxene during cooling, I knew that T_c becomes independent of the temperature specified for the onset of cooling (T_o) if there is a substantial difference between the two temperatures. For example, for the simulations of Fe-Mg ordering state in Opx shown in Figure 2.6a, the T_c remains independent of T_o as long as it is at least 50° C above the point of divergence of a simulated ordering path (solid line) from the corresponding equilibrium path (dashed line). In other words, if there were substantial diffusive readjustment of the ordering state prior to quenching, the ordering state would be independent of T_o . With this insight, I carefully read through the mathematical details of Dodson's paper, which are mostly in the Appendix – it took me a long time to completely understand the paper – and finally wrote a letter to Dodson pointing out that the validity of his formulation was limited to systems that had undergone



a critical amount of diffusive loss (small grain size, slow cooling rate or a combination of both), a point that no one seemed to have noticed in the nearly 25 years timespan and extensive use for a variety of systems since its publication.

I was not sure how Dodson was going to react; I had not met him before. However, his prompt e-mail response was very pleasant, and in which he presented, in his own words, a *“very much intuitive, physicist’s approach to the matter”*, hoping that *“it goes some way to answering”* my concerns. He further added that *“I plan during the next year to produce a 25 year review of the theory of closure temperature/closure profiles, which ought to clearly fill the gaps of this nature”* (i.e. my concern about the domain of validity). To one of my follow up e-mails, Dodson responded as follows. *“You raise some interesting points, to which I cannot yet give complete replies. Frankly, the convoluted mathematical arguments in my 1973 paper (I was picking my way through unfamiliar mathematical territory, with many twists and turns) are hard to follow at this distance of time! I do believe the approach in the 1986 paper is simpler to work with Another way of expressing the problem which you raise is to say that **calculated closure temperatures which come out close to the metamorphic temperatures are bound to be in error to some extent**”* [emphasis mine].

By “1986 paper”, Dodson referred to a paper that he had published in a *Materials Science* journal (!!) to which I referred in my e-mail discussion. This is not a journal that Earth scientists usually follow, and I do not recall how I came across that paper. It seems to me that being the gentleman that he was (see Section 1 on Dodson), Dodson stepped aside and left the problem to be handled by me, sensing from my e-mails that I should be able to do that. I immediately got to the task, in collaboration with my student, Max Tirone, and after some “twists and turns”, succeeded in coming up with the derivation of an expression of closure temperature that is valid for an “arbitrary extent of diffusion” The expression is as follows (Ganguly and Tirone, 1999).

$$\frac{E}{RT_c} = \ln \left(- \frac{A'RTD_o}{Ea^2 (dT / dt)_{@T}} \right) \quad (7.1)$$

Here E is the activation energy of diffusion of the species in a mineral, D_o is the pre-exponential factor in the expression of diffusion coefficient (D = D_oexp(-E/RT)), (dT/dt)_{@T} is the cooling rate at T that appears in the numerator, a is a characteristic dimensional parameter (radius for a sphere or a cylinder, and half-thickness for a plane sheet) and A' = exp(G + g), with G being a geometric factor with specific values for sphere (4.0066), cylinder (3.29506) and plane sheet (2.15821) (Dodson, 1973) and g a “memory” factor that is a function of M (see equation (7.2) for the latter). The mathematical expression of g was derived by Ganguly and Tirone (1999) and graphically illustrated as a function of M for the different geometries. Computer programmes for calculation of T_c according to the above expression as well as for other types of calculations discussed in the following section are



available from my webpage. Also, a comprehensive review of the topics discussed in this and following section, as well as the effects of modal abundance and nature of the matrix phase, may be found in Ganguly and Tirone (2009).

As emphasised by Dodson (1986), a mineral grain does not have a uniform or single closure temperature; instead, it has a closure temperature profile with a maximum at the core and minimum at the rim. This is because a mineral maintains equilibrium with the matrix down to a temperature that becomes progressively lower, moving from the core to rim, thus leading to a quenched concentration profile (Fig. 7.2) and a corresponding T_c -profile (the timescale of diffusive exchange or communication varies as the square of the distance). In the above expression, as well as in the one in Dodson's classic 1973 paper, the T_c is the weighted average of the spatially dependent T_c values. It was assumed by both Dodson (1973, 1986) and Ganguly and Tirone (1999) that the mineral grain was (a) homogenised at the onset of cooling with respect to the species of interest, and (b) surrounded by a homogeneous and effectively infinite matrix so that the matrix composition remained practically unchanged.

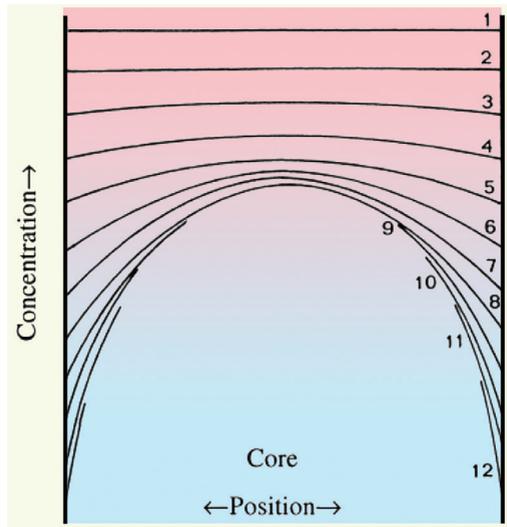


Figure 7.2 Successive concentration profiles of a species within a mineral grain as it cooled from a temperature at which its concentration profile was homogeneous. The surface of the grain maintained equilibrium with the matrix during cooling. The increasing curvature of the concentration profiles at progressively lower temperatures (1 → 12) is a consequence of the fact that the time scale of diffusive transport of the species to achieve equilibrium with the matrix became progressively longer as the mineral cooled. The quenched concentration profile is a collection of compositions that got quenched at different temperatures, increasing from the rim to the core. Modified from Dodson (1986).

The above expression for closure temperature is formally similar to the one in Dodson (1973). Although Dodson simply wrote (dT/dt) in the denominator of the ratio of terms in the right-hand side, it is actually a cooling rate at the specific T that appears in the numerator. Dodson wrote this T as T_c in which case the cooling rate in the denominator is at T_c (Dodson assumed the same asymptotic cooling model discussed in Section 2.4.1 and used to calculate the change of Fe-Mg ordering state in orthopyroxene during cooling, as illustrated in Fig. 2.6a).

Thus, in Dodson's equation, the unknown quantity T_c appears on both sides of the equation. For computational purposes, it is more straightforward to treat T on the right-hand side as the peak temperature, T_p , which is usually a known quantity and correspondingly to treat (dT/dt) as the initial cooling rate. Once the T_c is calculated, the cooling rate (CR) at T_c is easily found from the relation $CR(T_c)/CR(T_p) = (T_p/T_c)^2$ that follows from the adopted asymptotic cooling model. And, of course, a similar relation can be used to calculate cooling rate at any other T at which the asymptotic model may be expected to have remained valid.

The only, but not a minor, difference between the above expression and that in Dodson (1973) lies in the term A' . In the latter, A' lacks the "memory" factor (e^g) since Dodson assumed that the initial condition was "forgotten". This important assumption was not stated in words but was implicit in the detailed mathematical treatment in the Appendix that was not easy to follow. The memory function has a complicated expression (Ganguly and Tirone, 1999), and is a function of a dimensionless variable, M , that is given by

$$M = - \frac{RD(T_p)T^2}{E \left(\frac{dT}{dt} \right)_{@T} a^2} = \frac{RD(T_p)}{E\eta a^2} \quad (7.2)$$

where $D(T_p)$ is the diffusion coefficient at the peak temperature at the onset of monotonic cooling. Physically, the square root of M may be viewed as an integrated diffusion distance normalised by the characteristic dimension of a grain, a .

An example of the calculation of (weighted average) T_c as a function of cooling rate, grain size and T_p , according to equation (7.1) is shown in Figure 7.3 which is modified from Ganguly *et al.* (1998). Here the T_c refers to the closure temperature of the Sm-Nd decay system in almandine garnet and was calculated using the diffusion data in Ganguly *et al.* (1998). The dashed lines in the figure represent calculations according to Dodson (1973) that are independent of T_p . Let us now consider a spherical garnet grain of 1.5 mm radius that cooled at a rate of 10 °C/Myr from a peak temperature of 700 °C. The T_c of this grain, according to equation (7.1), is 680 °C, but is 725 °C according to the Dodson (1973) formulation, exceeding the prescribed T_p . The problem of T_c exceeding T_p that has been found earlier using the Dodson formulation is due to its application beyond its domain of validity. This domain is defined by the value of M at which the "memory factor" g becomes negligible. The g vs. M relations for different geometries have



been calculated and illustrated by Ganguly and Tirone (1999) and presented in a graphical form. The T_c vs. cooling rate curves calculated from the Dodson formulation coincide with those calculated from the equation (7.1) for slow cooling rates, depending on the grain size, where $g \approx 0$ ($M \geq 1$).

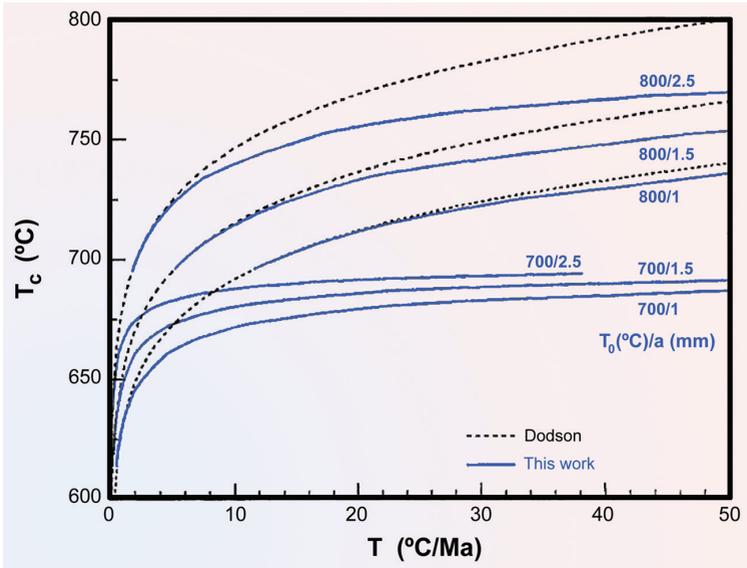


Figure 7.3

Closure temperature (T_c) of the Sm-Nd decay system in spherical garnet grains as a function of temperature (T_0) at the onset of cooling, grain radius (both shown as numbers on the curves) and cooling rate, \bar{T} . The compositions of Sm and Nd have been assumed to be homogeneous at T_p . Modified from Ganguly *et al.* (1998).

7.2 Cooling Rate from Resetting of a Mineral Age

As an extension of the above work on the closure temperature of a decay system in a mineral, we came up with methods for determining the cooling rate of a rock from (a) the extent of resetting of the bulk age of a mineral according to a specific decay system during cooling, and (b) the age profile in a mineral according to a decay system that is a consequence of its T_c profile resulting from the position dependent diffusive closure of the species of interest within a mineral grain (Fig. 7.1). These methods are discussed below. Even at the cost of redundancy, I would like to re-emphasise that a cooling rate derived resetting of a decay system is applicable only to a limited range of temperature around its T_c .



7.2.1 Cooling rate from resetting of a bulk mineral age

When the age of a mineral according to a specific decay system (e.g., Sm-Nd age of garnet) is determined from isotopic analysis in a mass spectrometer using solutions of grains separated from a rock, one determines the bulk age for the average grain size in the aliquot. If this mineral age is lower by Δt from the peak metamorphic age determined on the basis of whole rock isotopic data or by a decay system such as U-Pb for which the mineral age is not susceptible to significant resetting during cooling owing to the very slow diffusivity of the decay product, then it can be shown that (Ganguly *et al.*, 1998; Ganguly and Tirone, 2001, 2009)

$$\Delta t = \frac{R}{\eta E} (\ln M + G + g) \quad (7.3)$$

One can calculate the right-hand side from a knowledge of the diffusion coefficient of the decay system within the mineral of interest and specifying peak temperature, grain size, grain geometry and the cooling time constant, η . The procedure is repeated by varying η until the calculated Δt matches the observed resetting of the decay system in the mineral. Here η is calculated from an assumed cooling rate (differentiation of the adopted asymptotic form of T-t relation yields $dT/dt = -\eta T^2$), M is calculated according to equation (7.2) and g is determined according to Ganguly and Tirone (1999) or from the tabulated values (Ganguly and Tirone, 2001) of bulk g as a function of M and crystal geometry.

As an example of the application of this method, let us consider the study by Ganguly *et al.* (1998), who calculated the cooling rate of a sample from the Archean Pikwitonei Granulite Domain of the superior province, Canada. Using two-feldspar thermometry, Mezger *et al.* (1992) estimated $T_0 \approx 750$ °C for the peak metamorphism at ~2640 Ma that was determined by U-Pb ages of zircon and garnet. They also determined the Sm-Nd age of garnet crystals with apparent diameter, as observed in a thin section, varying between ~1 and 5 mm and found it to be 30 Myr younger than the U-Pb age. Using these data and the diffusion parameters of the daughter product, Nd, that is almost the same as that of Sm, Ganguly *et al.* (1998) determined a cooling rate of ~2-4 °C/Myr at T_c . This result is in excellent agreement with the cooling rate deduced by Mezger *et al.* (1992) (~2 °C/Myr) from the conventional T_c vs. mineral age plot of multiple systems, such as in Figure 7.1.

Shortly after the publication our 1998 paper, I met someone (now well known in the geochronology community – name withheld intentionally) in a conference who told me that he had used our method of determining the cooling rate from the age resetting of a single mineral in his doctoral dissertation, but had a hard time convincing his adviser about the validity of the method. It may be understandable since no geochronologist had taken this approach before and it came from a group way outside the mainstream of the subject. It is, however, yet another example of the fact that new ideas in a field sometimes come from people who are not established practitioners in that field.



7.2.2 Cooling rate from age profile within a mineral

Ganguly and Tirone (1999) discussed a method of calculation for a cooling age profile of a mineral as a function of the dimensionless parameter M (equation (7.2)) so that the cooling rate of a mineral could be determined if one could measure its cooling age profile by finding a match with a simulated profile. However, asking for determination of a cooling age profile is a tall order. Thus, Ganguly and Tirone (2001) developed a more practical approach, building on their earlier work, so that one can determine the cooling rate of a mineral from the difference ($\Delta\Gamma$) between its bulk age and the age of a spatially averaged central segment according to a single decay system. The relation to be used readily follows from the last equation and is as follows;

$$\Delta\Gamma = \frac{R}{\eta E} (\Delta G + \Delta g) \quad (7.4)$$

where Δ stands for the difference of the specified quantity between its weighted average values at a central domain and for the bulk crystal. The values for G and g , averaged over the normalised radial distances of 0.25, 0.50 and 1.00 (referred to as $G(x)$ and $g(x)$) for different geometries were presented by Ganguly and Tirone (2001) in tabular forms. The computed relation between $\Delta\Gamma$ and η for a grain of spherical geometry and with specified values of M are illustrated in Figure 7.4 (recall that g is a function of both x and M). Additional calculations for the cylindrical and plane sheet geometries can be found in Ganguly and Tirone (2001).

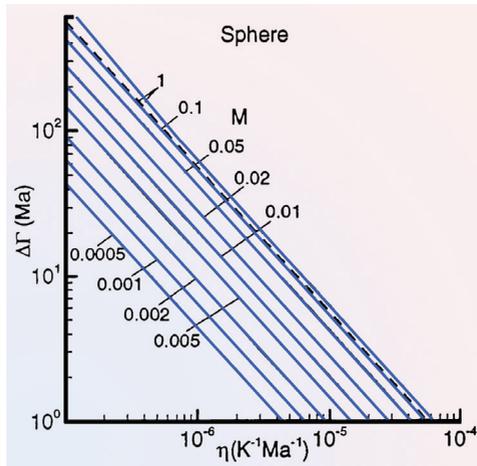


Figure 7.4

The difference between the average age of core or a central segment and bulk age ($\Delta\Gamma$) of a spherical grain as a function of the cooling time constant, η , and the dimensionless variable, M (equation (7.2)). The solid and dashed lines apply to $\Delta\Gamma$ with core ages over $x = 0.5$ and 0.25 , respectively, where x is the radial distance normalized with respect to the radius of the grain. There is no significant difference between these two ages for $M \leq 0.05$. Modified from Ganguly and Tirone (2001).



The above approach was followed by Ducea *et al.* (2003) to calculate the initial cooling rate of 4-13 °C/Myr of a large garnet crystal (Fig. 7.5) embedded within a biotite matrix from the metamorphic core complex in Valhalla, British Columbia (Spear and Parrish, 1996). They also determined the cooling rate of the same garnet crystal from the retrograde zoning profile of Mg that is qualitatively similar to the profile illustrated in Figure 2.8. Diffusion kinetic modelling of the data yielded an initial cooling rate of 2-13 °C/Myr, which is in excellent agreement with that retrieved from the difference between the core and bulk Sm-Nd ages. In contrast to these results, Spear and Parrish (1996) calculated cooling rate of 24 (± 6) °C/Myr for the Valhalla rocks using the conventional T_c vs. age plot of multiple geochronological systems that is illustrated in Figure 7.1. Here each geochronological system was assumed to have a unique range of T_c for a given mineral. A consensus number for the cooling rate, as suggested by Ducea *et al.* (2003), may be ~15-20 °C/Myr.

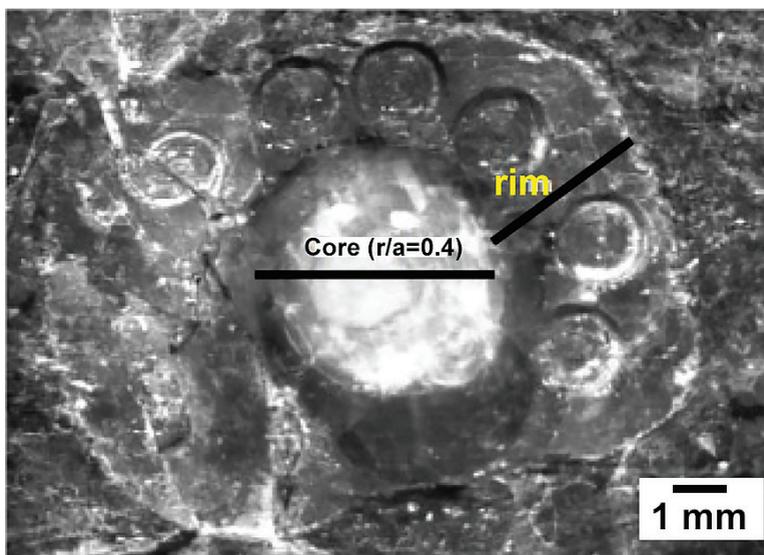


Figure 7.5 Photograph of the garnet crystal, embedded in a biotite matrix, from the Valhalla complex, British Columbia, after the core region was milled out during the process of rim extraction. The drilled pits were ~130 μm deep. Modified from Ducea *et al.* (2003).

7.3 Differential T_c -s of Parent and Daughter Nuclides and Implications

In the determination of the age of a sample from its mineral isochron, it is implicitly assumed that the diffusive transport of the parent nuclide into or out of the mineral grains had effectively ceased at or before the T_c of the daughter nuclide.



However, this requirement may not be satisfied when the parent nuclide has lower valence state than the daughter nuclide. I consider here two important decay systems, namely the $^{176}\text{Lu}^{3+}$ - $^{176}\text{Hf}^{4+}$ and $^{53}\text{Mn}^{2+}$ - $^{53}\text{Cr}^{3+}$, for which we have determined the diffusion coefficients and explored their implications for dating of garnets in metamorphic rocks and high temperature thermochronology of meteorites.

7.3.1 ^{176}Lu – ^{176}Hf dating of garnet

^{176}Lu decays to ^{176}Hf by the process of β -decay and has a half-life ($t_{1/2}$) of 37.1 Gyr. This decay system has been widely used for garnet-whole rock (WR) geochronology of terrestrial rocks, often in conjunction with the ^{147}Sm - ^{144}Nd (α -decay; $t_{1/2} = 106$ Gyr) system. For the Sm-Nd system, the diffusivities of both ionic species been found to be effectively the same (Ganguly *et al.*, 1998), as one should expect based on the fact that both are in the trivalent state within a crystal and have similar ionic radii (1.079 for Sm^{3+} vs. 1.109 Å for Nd^{3+} in the 8-fold coordination in garnet). However, one would expect that owing to its higher valency, the diffusivity of Hf^{4+} within garnet (or in general within a crystal) to be slower than that of Lu^{3+} . The smaller ionic radius in an 8-fold coordination of Hf^{4+} (0.83 Å) relative to that of Lu^{3+} (0.977 Å) might have a compensating effect on the relative diffusivities, but still Hf^{4+} may have a significantly slower diffusivity than Lu^{3+} . Based on these crystal chemical considerations, we undertook a thorough investigation of the diffusion kinetic properties of Lu and Hf in garnet. And this was a very challenging project for multiple reasons.

Eli Bloch came on board as a graduate student at the right time. He was a semi-professional drum player who dropped out of academia after high school, but later returned to the University of Washington to finish his B.S. degree in Geology with Stuart McCallum, my fellow graduate student from Chicago, as his mentor. Eli got offers from some other highly respected schools but finally decided to work with me. As I later understood from him, one of the reasons behind this decision was that I was the only one who did not follow up his campus visit by a phone call or an e-mail! Eli had long hair that gave him the look of a rock musician and was quite active with his music groups even after he started his graduate studies; so, I was a bit unsure if he would continue. After a few months, my late colleague Clem Chase dropped by my office and asked me if I had seen Eli that day. When I replied that no, I had not, Clem told me that Eli had cut his hair short and he thought that it was an indication that Eli had finally made the commitment for the hard life of a graduate student, moving away from the fun filled days with music groups.

As anticipated, the diffusivity of Hf^{4+} in garnet turned out to be much slower than that of Lu^{3+} (the diffusivities of both are much slower than those of Sm and Nd). Bloch *et al.* (2015) calculated the consequent closure temperatures of the two nuclides according to the modified Dodson formulation due to Ganguly and Tirone (1999). The closure temperatures and closure intervals (I_c) of Lu and



Hf in garnet are illustrated in Figure 7.6 as functions of T_p , radius of spherical garnets (r) and cooling rates, \dot{T} . The I_c denotes the time interval between the closure temperatures of Hf and Lu for specific values of T_o , r and \dot{T} .

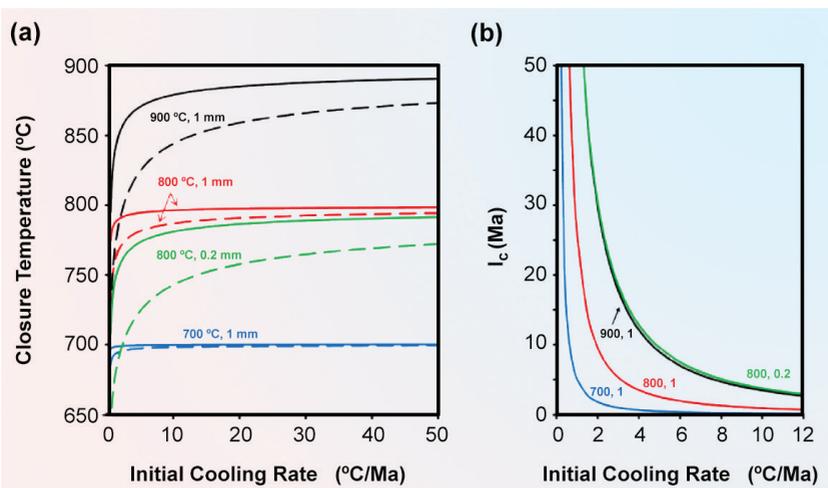


Figure 7.6 (a) Closure temperatures and (b) closure intervals (I_c) of Lu and Hf in garnet as functions of peak temperature (T_p), radius of spherical grains (r) and cooling rates (\dot{T}). I_c denotes the time span between the Lu and Hf closure temperatures for specific values of T_o , r and \dot{T} . In the panel (a), the solid lines are for Hf and the dashed lines are for Lu.

It is a common knowledge in the petrology-geochronological community that in metapelites, the Lu-Hf garnet-whole rock (Grt-WR) ages are often significantly older than their Sm-Nd ages. These discrepancies between the Lu-Hf and Sm-Nd ages of garnet are largely due to the greater diffusive resetting of the Sm-Nd system relative to the Lu-Hf system in garnet. An additional contribution to the older Lu-Hf ages of garnet stems from the preferential retention of ^{176}Hf relative to the parent nuclide ^{176}Lu in garnet (due to the much slower diffusivity of Hf relative to Lu) during the thermal evolution experienced by the host rock. It was suggested by Kohn (2009) that the continued diffusive loss of Lu from garnet crystals to the matrix phases in a metapelite between $T_c(\text{Hf})$ and $T_c(\text{Lu})$ in garnet might cause an anticlockwise Grt-WR “isochron” rotation relative to the case where the garnet crystals remained effectively closed at $T \leq T_c(\text{Hf})$; consequently, the Lu-Hf age of a metapelite garnet would appear to be older than its Sm-Nd age.

Using the experimentally determined diffusion data, Bloch and Ganguly (2015) carried out detailed numerical simulations of the effect of differential diffusivities of Lu and Hf in garnet on the development of Grt-WR isochrons in metapelite and metabasic rocks along prescribed T-t paths. The simulations



involved consideration of garnet nucleation and growth in the prograde path and development of bell-shaped compositional zoning of Lu in garnet using Rayleigh fractionation model between garnet crystals and the matrix. Thermodynamic analysis suggests that the garnets in metapelites would lose Lu to the matrix phases during cooling whereas the opposite may be true for some metabasic rocks. For their simulations, Bloch and Ganguly (2015) deduced a range of plausible partitioning behaviour of Lu between garnet and matrix phases as a function of temperature; they used the simplified scenario that Lu partitioning in the garnet-biotite and garnet-clinopyroxene (Cpx) systems essentially capture the garnet-matrix partitioning behaviour in the metapelitic and metabasic rocks, respectively.

The simulations show that Lu-Hf Grt-WR ages are sometimes spurious in that they do not relate to any specific marker event during the thermal evolution of a rock, such as nucleation of garnet, end of garnet growth, attainment of peak temperature, closure of Hf or Lu during cooling. In contrast, the simulations show that the Sm-Nd age of garnets records the time lapse since the T_c (Nd) or the so called cooling age, regardless of the bulk composition of the rock. This simplicity stems from the fact that both the parent and daughter nuclides have nearly identical diffusivities and effectively the same closure temperatures in garnet for a prescribed set of T_p , grain size and T-t path.

The contrasting behaviour of the Sm-Nd and Lu-Hf systems in a metapelitic garnet are illustrated by numerical simulations in Figure 7.7, using a crystal of 0.25 mm radius. The panel (a) shows a prescribed T-t path with a total time span of 1020 Myr since the nucleation of garnet while the panels (b) and (c) illustrate, respectively, the evolutions of the $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ vs. $^{176}\text{Lu}/^{177}\text{Hf}$ ratios in the garnet. The Grt-WR isochrons at the end of the simulations are illustrated by dashed lines in both figures. The simulated Grt-WR age for the Sm-Nd system, which is 918.6 Ma (panel (b)), is marked in the T-t path (panel (a)) by a filled circle. This is a cooling age and is almost identical to that corresponding to the time lapse since the closure temperature of the decay system in the garnet, as calculated from the modified Dodson formulation (equation (7.1)) due to Ganguly and Tirone (1999). On the other hand, the simulated Grt-WR Lu-Hf age, which is 1030.5 Ma (panel (c)) is older than even the prescribed nucleation age of garnet. Similar simulation along the same T-t path but using the Lu partitioning behaviour in the Grt-Cpx pair as a proxy for that between garnet and matrix in a metabasic rock yields a Grt-WR Lu-Hf age of 999.3 Ma that is younger than the Sm-Nd cooling age. Thus, it is possible that in some metabasic rocks, the Lu-Hf garnet age may post-date its Sm-Nd age.



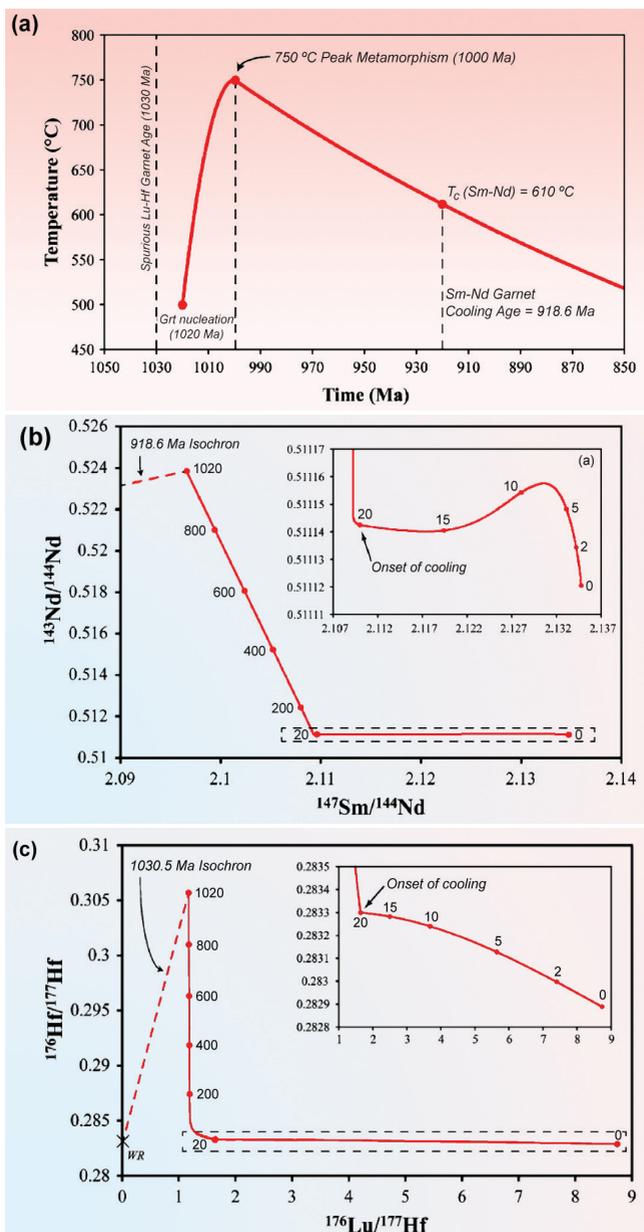


Figure 7.7

(a) A prescribed T-t path, (b) and numerical simulations of the evolution of the isotopic ratios of the Sm-Nd and (c) Lu-Hf systems in a garnet crystal of 0.25 mm



radius within a metapelite with prescribed values of the initial isotopic ratios. The dashed lines (b) and (c) show the Grt-WR isochrons at the end of the simulations whereas the markers on the growth curves of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ indicate the elapsed time in My since garnet nucleation. The inset shows enlargements of the horizontal segments marked by dashed boxes.

Bloch and Ganguly (2015) carried out many other simulations on the evolution of the Lu-Hf zoning profile and Lu and Hf isotopic ratios in garnets. A general conclusion that emerges is that the bell-shaped growth zoning of Lu and the consequent bell-shaped zoning of the decay product (^{176}Hf) might have remained partially preserved in many metamorphic rocks through the duration of the peak thermal condition. Thus, the Lu-Hf Grt-WR ages would not necessarily correspond to the time lapse since the closure of the Lu-Hf decay system within the garnet crystals because part of the measured ^{176}Hf could have been inherited from the prograde period. For garnets with radius of ± 0.5 mm and $T_p \leq 700$ °C, Lu-Hf Grt-WR age would usually reflect a time lapse from some intermediate state between garnet nucleation and maximum growth.

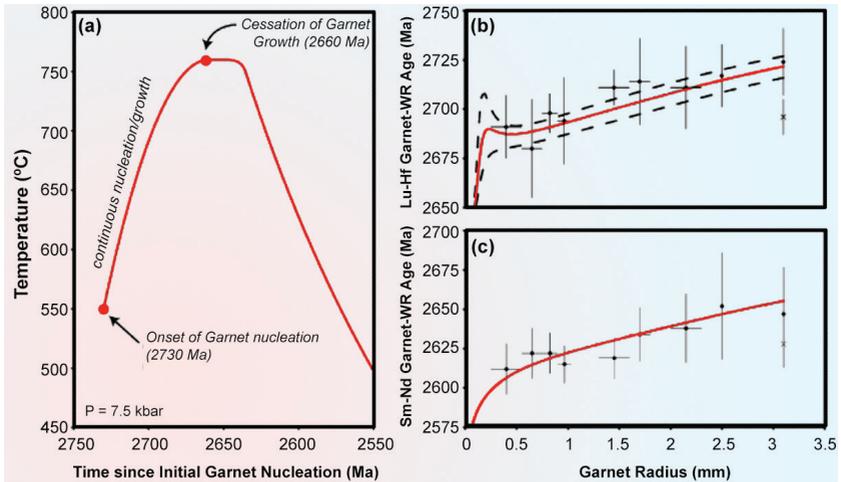


Figure 7.8

Grain size dependent ^{176}Lu - ^{176}Hf and ^{147}Sm - ^{143}Nd ages of garnets from the Pikwitonei granulite domain reported by Smit *et al.* (2013) and those predicted by a numerical model that incorporated garnet nucleation and growth along a prescribed T-t path, fractionation of elements with the matrix and evolution of the two decay systems. (a) A metamorphic T-t path (with formal T-t relations for pro- and retrograde paths), for which the peak P-T condition was constrained by thermobarometry, showing the onset of garnet nucleation and cessation of garnet growth; (b) and (c) show the predicted grain size dependent Lu-Hf and Sm-Nd ages (lines) and comparison with those (symbols) determined by Smit *et al.* (2013).



It has been shown by Bloch and Ganguly (2015) that the discrepant Lu-Hf and Sm-Nd ages of garnet could be used, *via* numerical simulation, to reconstruct the thermal history of a metamorphic rock if there are independent constraints on the peak temperature and cooling rate. This method was applied to model the grain size dependent Lu-Hf and Sm-Nd garnet ages of metapelites from the Pikwitonei granulite domain, Canada (Smit *et al.*, 2013). The results are illustrated in Figure 7.8. It was assumed that the rocks experienced a single thermal pulse. Following this approach, Ibanez *et al.* (2018) used the discrepant Lu-Hf and Sm-Nd ages of garnet (of the same average grain size and determined from the same aliquot) along with independent constraints on the peak temperature and cooling rate of a sample from the collisional metamorphic terrane in the Proterozoic Putumayo orogen of Amazonia to reconstruct its thermal history. The Lu-Hf Grt-WR age of the sample was found to pre-date the garnet nucleation age prescribed in the successful simulation that reproduced the observed discrepancy between the Lu-Hf and Sm-Nd ages of garnet (this scenario is similar as that illustrated in Fig. 7.7c). The simulated garnet growth period was found to be ~25 Myr.

7.3.2 $^{53}\text{Mn} - ^{53}\text{Cr}$ cosmochronology

The $^{53}\text{Mn} - ^{53}\text{Cr}$ decay system, in which ^{53}Mn decays by electron capture to ^{53}Cr ($t_{1/2} = 3.7$ Myr), has been widely used in the study of relative age sequence of the early solar system objects or events according to the relation (Birck and Allègre, 1988).

$$\Delta t = \frac{1}{\lambda_{\text{Mn}}} \ln \frac{\left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}} \right)_o^{\text{I}}}{\left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}} \right)_o^{\text{II}}} \quad (7.5)$$

where Δt is the age difference between the samples I and II, λ_{Mn} is the decay constant of ^{53}Mn ($0.187337 \text{ Myr}^{-1}$), ^{55}Mn is the stable isotope of Mn, and the subscript o stands for the initial Mn isotopic ratio at the time of closure of Cr diffusion in the system. The relative age may be converted to an absolute age if one of the two samples has a well defined age based on some other decay system. Usually this “anchor” sample is one of the rapidly cooled angrites¹⁹, LEW86010 and D’Orbigny, that have well defined Pb-Pb ages of $4558.55(\pm 0.14)$ and $4564.42(\pm 0.22)$ Ma, respectively. It is assumed that owing to the rapid cooling, both Pb-Pb and Mn-Cr systems had closed effectively at the same temperatures in these samples.

It can be shown (*e.g.*, Posner *et al.* 2016) that the slope of an ϵ_{Cr} vs. $^{55}\text{Mn}/^{52}\text{Cr}$ plot defined by the data of mineral separates from a sample, such as illustrated in Figure 7.9, yields the $(^{53}\text{Cr}^*/^{55}\text{Mn})_t$ ratio of the minerals where Cr* is the radiogenic

19. Angrites are a rare group of achondrites (*i.e.* stony iron meteorites that are devoid of chondrules) consisting primarily of clinopyroxene, augite, and some olivine, Ca-rich plagioclase and troilite.



Cr produced during the elapsed time (t) since $T_c(\text{Cr})$. Here ϵ_{Cr} is the conventional epsilon representation of $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of a mineral relative to a standard. Now if the mineral grains used in a Mn-Cr isochron plot did not suffer any diffusive gain/loss of ^{53}Mn below its $T_c(\text{Cr})$, then we have $(^{53}\text{Cr}^*/^{55}\text{Mn})_t = (^{53}\text{Mn}/^{55}\text{Mn})_0$ (i.e. all $^{53}\text{Cr}^*$ were produced only by the decay of ^{53}Mn that was present within a mineral grain at $T_c(\text{Cr})$).

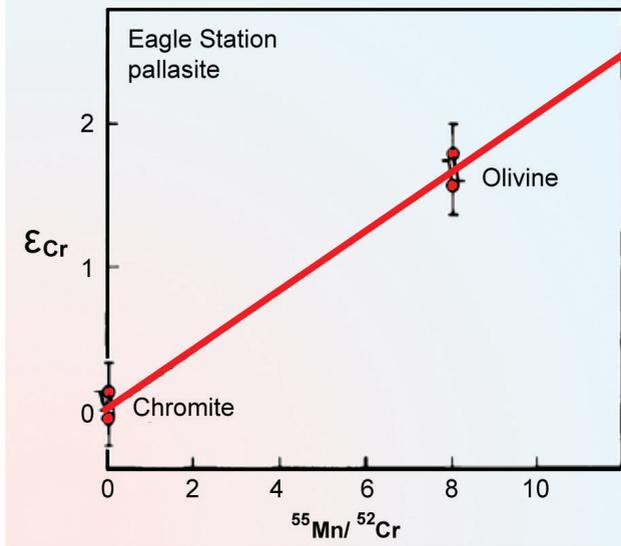


Figure 7.9 An example of a $^{53}\text{Mn} - ^{53}\text{Cr}$ isochron diagram. The sample is from the Eagle station pallasite for which a two-point isochron is defined by the Cr isotopic compositions and $^{55}\text{Mn}/^{52}\text{Cr}$ ratios of chromite-spinel and olivine separates. Modified from Birck and Allègre (1998).

We have determined the diffusion kinetics of Cr in olivine (Ito and Ganguly, 2006), orthopyroxene (Ganguly *et al.*, 2007) and spinel (Posner *et al.*, 2016) and calculated, using the diffusion data, the $T_c(\text{Cr})$ in the minerals as a function of T_p , grain size and cooling rates, accounting for the diffusion anisotropy in the non-cubic minerals. The T_c -s were calculated according to the modified form of Dodson's formulation due to Ganguly and Tirone (1999) (equation (7.1)). Posner *et al.* (2016) also calculated the $T_c(\text{Mn})$ in spinel, assuming that the diffusion coefficient of Mn^{2+} , $D(\text{Mn}^{2+})$, in spinel is similar to its $D(\text{Fe}^{2+})$ that was determined by Liermann and Ganguly (2002). As argued by Posner *et al.* (2016), the assumption of similarity of $D(\text{Mn}^{2+})$ and $D(\text{Fe}^{2+})$ is very reasonable since the Fe and Mn are the nearest neighbours in the transition metal series and have similar ionic radii ($r(\text{Mn}^{2+}) = 0.66 \text{ \AA}$ and $r(\text{Fe}^{2+}) = 0.63 \text{ \AA}$ in the four-fold coordination in spinel in their high spin states). Additionally, it may be noted that these two ions have

nearly ideal mixing properties and equal diffusivities in garnet (Ganguly *et al.*, 1996; Chakraborty and Ganguly, 1992), as expected from their crystal chemical similarities.

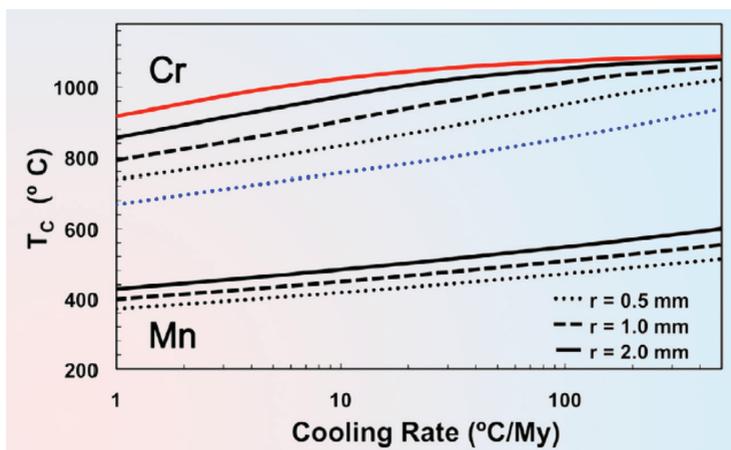


Figure 7.10 Comparison between the closure temperatures (T_c) of Cr and Mn diffusion in spherical grains of spinel (with the radius values specified within the figure) that cooled from a temperature (T_p) of 1100 °C. For $T_c(\text{Cr})$, all but the top (red) and bottom (blue) curves have been calculated using $D(\text{Cr})$ at wüstite-magnetite buffer $f(\text{O}_2)$ conditions and $\text{Cr}\# \sim 0$. For the top (red) curve the $D(\text{Cr})$ is that corresponding to three orders of magnitude lower $f(\text{O}_2)$. The dotted blue curve represents estimated $T_c(\text{Cr})$ for $\text{Cr}\# \sim 1.0$ ($r = 0.5$ mm). The $f(\text{O}_2)$ for the $D(\text{Mn})$ data are those corresponding to the graphite buffer, which is below iron-wüstite buffer at $T > 600$ °C at 1 bar total pressure. All T_c values were calculated according to equation (7.1). Modified from Posner *et al.* (2016).

The calculated closure temperatures of Cr and Mn diffusion in spinel, which are illustrated in Figure 7.10, suggest that spinel and quite likely other mineral grains in a meteorite sample could have remained open to diffusion of Mn for a few hundred degrees below $T_c(\text{Cr})$. To appreciate the potential consequence of this differential closure temperatures of Cr and Mn, let us first consider the relationship between $(^{53}\text{Mn}/^{55}\text{Mn})_o$ and $(^{53}\text{Cr}^*/^{55}\text{Mn})_{t'}$ during the closure interval between Cr and Mn diffusion, $\Delta T_c(\text{Cr-Mn})$, in an isolated mineral grain (Posner *et al.*, 2016).

$$\left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}}\right)_o = \left(\frac{^{53}\text{Cr}^*}{^{55}\text{Mn}}\right)_{t'} + \left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}}\right)_{t'} \quad (7.6)$$

Here t' indicates an elapsed time since $T_c(\text{Cr})$ of a mineral whereas the first and last terms on the right indicate, respectively, the growth of $^{53}\text{Cr}^*/^{55}\text{Mn}$ during t' and the residual $^{53}\text{Mn}/^{55}\text{Mn}$ at t' . Since it was produced at $T < T_c(\text{Cr})$, the $^{53}\text{Cr}^*$ in the mineral grain would not have suffered from any diffusive loss/gain. However,



the requirement of thermodynamic equilibrium between two minerals within $\Delta T_c(\text{Cr-Mn})$ requires Mn exchange, both isotopic and elemental (e.g., $^{53}\text{Mn}(\text{Spnl}) + ^{55}\text{Mn}(\text{Ol}) = ^{55}\text{Mn}(\text{Spnl}) + ^{53}\text{Mn}(\text{Ol})$; $\text{Mn}(\text{Spnl}) + \text{Fe}(\text{Ol}) = \text{Fe}(\text{Ol}) + \text{Mn}(\text{Spnl})$), with the former leading to almost exactly the same $^{53}\text{Mn}/^{55}\text{Mn}$ ratio in both minerals within the closure interval. This process would affect both terms on the right of the above equation and thus lead to some error in the inferred initial ($^{53}\text{Mn}/^{55}\text{Mn}$)_o. It, however, remains to be evaluated by numerical simulations as to what extent the differential closure temperatures of Cr and Mn in minerals might have compromised their Mn-Cr ages of meteorite samples determined by following the conventional approach that ignores the problem of diffusive exchange of Mn post- $T_c(\text{Cr})$.

Posner *et al.* (2016) showed that for reasonable planetary scenarios (cooling rate 5-125 °C/Myr at $T_c(\text{Cr})$ with the T-t relation following the asymptotic form given in Section 2.4.1), the characteristic length scale of Mn diffusion in spinel is 2-3 mm within the half-life (3.7 Myr) of ^{53}Mn . This suggests that spinel grains could have been vulnerable to diffusive exchange of Mn post- $T_c(\text{Cr})$. Disturbed Mn-Cr ages in meteorites have been reported by Papanastassiou *et al.* (2005) and Göpel *et al.* (2015). As discussed by Posner *et al.* (2016), these disturbed ages might have been due to the open system behaviour of Mn within the closure interval of Cr and Mn.



In this volume, I recounted my personal journey in the fields of thermobarometry and high temperature thermochronology along with a narrative of the historical developments in these fields. In this long journey, I witnessed how the synergetic growth of thermodynamics, experimental studies at high P-T conditions and calorimetric studies had fundamentally transformed how we look at and think about rocks and exposures. Later diffusion kinetic studies and heat transfer modelling joined forces to enable expansion of the quantitative domain of petrology. The field has now progressed even further *via* sophisticated numerical modelling and incorporation of fluid dynamics.

Initially, the impetus to learn thermodynamics in the petrology community came from the desire to put quantitative constraints on the state conditions (P-T-fluid composition) experienced by rocks through their evolutionary histories after it was demonstrated that thermodynamics is indeed applicable to complex natural systems. The practitioners had to do their own calculations and that, of necessity, required them to have a fairly good background in classical thermodynamics. Formal courses on the latter were almost completely lacking in the Geology departments of the time and thus we were sent out to chemistry or other departments, physics included, to acquire the exposure and training in thermodynamics. However, the content of those courses included much more than thermodynamics of phase equilibrium as they were meant for the students in other disciplines who required a wider exposure and knowledge of the subject; in some cases, the course material had other fundamental science components beyond thermodynamics. Thus, in order to get good grades, we were forced to study materials that did not quite seem to be relevant to petrology or geology at the time without asking the question "*why am I doing this?*" This, however, paid dividends in the long run as may be appreciated from the examples of some of my own work that I have discussed in this article.

A major transition in the field of metamorphic petrology took place around the turn of the millennium with the development of software packages for thermobarometric and phase equilibrium calculations. These packages, which I have discussed in this article, enabled people with virtually no knowledge of thermodynamics to carry out complex phase equilibrium calculations and apply them to deduce the conditions experienced by the rocks that they are dealing with. From a practical point of view, this is a major step forward that brought thermodynamic tools to a much larger user group. I greatly admire the developer of the software packages not only for their work but also for making them available to the community without seeking any financial benefit. However, development of these packages also has some unintended consequences that ironically are detrimental to the progress of the field.



First, the software packages seem to have disincentivised to a significant extent the learning of thermodynamics in the petrology community. Software packages for phase equilibrium calculations had been available in the field of materials sciences even before they were introduced in Geology (and these software packages have large commercial markets), but that did not lead to the disappearance of thermodynamics courses from their curricula. I have discussed, with real world examples, that use of the computational packages as black boxes may lead to pitfalls (this is true of any black box), and how individual thermobarometry (ITB) can, in many cases, provide a better and more direct path to the calculation of the state conditions experienced by a rock. I would further like to reiterate the point, which I have already made using examples, that a researcher would be in a better position to make judicious and more effective application of the software packages if he/she has good knowledge of classical thermodynamics, and physical chemistry in general. Aside from benefits for thermobarometric studies, a solid grounding in these fundamental sciences enables one to adapt to the changing frontiers of petrology-geochemistry and also to branch off in new directions; it cannot be overemphasised that a long career in research and teaching, one has to avoid stagnation and be in a position to explore bold new directions.

Another unintended consequence of the availability of the software packages has been in their effect in the field of experimental studies related to phase equilibrium relations and solution or mixing properties of minerals. I have found some younger people reluctant to be engaged in this type of research as they are afraid that their data will be “swallowed” by the internally consistent databases that are used in the software packages almost immediately after they appear in print. Whether we like it or not – I do not like it –, citation statistics have become important in many professional decisions. (It is a notable departure from the good old days, when people used to read a paper to judge its importance and intellectual content.) Thus, there has to be a way to give credit in terms of citation statistics to the original workers who put in the hard work. And that does not seem to me to be a particularly difficult task.

An important future direction in low temperature palaeothermometric studies lies in the integration of robust experimental data with DFT-based calculations within the framework of statistical thermodynamics. I have discussed the usefulness of this approach for hydrogen isotope fractionation in some mineral-water systems. It can be extended to other systems and perhaps also to oxygen isotope thermometry.

Integration of diffusion kinetics and geochronology offer a powerful approach to deciphering thermal history of rocks with an absolute time axis. I envision this approach, which I have discussed in this article, to be an important new direction in the field of thermochronology. The concept of closure temperature that is at the heart of the field is a very useful one but the notion of a fixed closure temperature of a decay system in a mineral is not. One should be careful to check if the conditions imposed in the derivation of the analytical expressions of closure temperature are satisfied by the sample that one is dealing with. In



addition to the effects of cooling rate, grain size (and initial temperature for slowly diffusing systems), closure temperature of a decay system in a mineral is affected by the abundance and nature of the matrix phases. Furthermore, there are problems in the determination and interpretations of ages when the closure temperature of a parent nuclide falls significantly below that of the daughter nuclide; these problems need to be addressed using an integrated approach involving diffusion kinetics.

I have shared two stories about the review and editorial handling of two of my papers. The history of science has many stories where seminal contributions were rejected and finally rescued after they were brought to the notice of some stalwarts; however, it is likely that some also got buried. Even though they do not belong to the same league, I hope that my stories would provide some food for thought for the editorial and review processes, especially for the papers of young scientists who are trying to break into a field. I happened to be one of the lucky ones, but survival of early career scientists should not have to rely on the fortuitous intervention and support of some stalwarts.



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