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JOHN H. JONES

Thoughts and Reminiscences on Experimental Trace Element Partitioning



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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Experiment JJ/IC-84 of J. Jones and I. Casanova for solid-metal/liquid-metal partitioning of As at 1250 °C in the Fe-Ni-S system. Vermiform bright regions are Fe-Ni metal. Yellowish interstitial regions are quenched sulphides, containing bright flecks of quenched metal dendrites. Black spots are plucks from the polishing process.

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THOUGHTS AND REMINISCENCES ON EXPERIMENTAL TRACE ELEMENT PARTITIONING

ABSTRACT

This perspective is a very personal account of the history and evolution of experimental trace element partitioning, although I cannot hope to exhaustively cover all aspects of this discipline. Therefore, I emphasise issues with which I am most familiar: (i) partitioning between mafic silicates and silicate melt; (ii) solid metal-liquid metal partitioning – especially the effects of non-metals; and (iii) metal-silicate liquid partitioning. I first entered the field of experimental partitioning as a grad-student in the mid-1970's and so was able to see some of the growing pains of this discipline up close and personal. Also where appropriate, I will mention applications of experimental partitioning data to geologic and planetary problems.



1.1 A Starting Point

This perspective is mainly written with graduate students in mind. I can remember as a grad-student walking home one night from Caltech (Pasadena, CA), in the dark, thinking about the thermodynamics underlying trace element partitioning. I thought I knew the basic thermodynamic equations, but I couldn't convince myself that I knew what they meant, physically. And there seemed to be no expert guidance on the subject; there were no books. Intuitively, I believed I knew the answer, but I also knew that I couldn't prove it. As a grad-student, I knew that anything I couldn't prove would never get me through my Ph.D. defense. So that was a problem. My temporary solution was to keep thinking about the issue, but to keep most of my ideas to myself. This very conservative approach turned out to be successful. I graduated. I then had a license to practise.

I have since then led multiple scientific lives: trace element partitioning, studies of siderophile elements & core formation, experimental petrology & phase equilibria, critiques of isotope chronologies, calculation of planetary compositions, and various studies of Mars, the Moon, and asteroidal basalts. Recently, I have started describing myself as a jack-of-all-trades, master-of-none. I think that is a fairly honest description. However, this contribution will focus only on trace element partitioning; the others are not my present charter. Therefore, some readers may perhaps not recognise me in this current guise. Where other studies overlap with the theme of this contribution, I will attempt to mention them. But for the most part, these other studies must be left for another day.

I will also try to give personal perspectives of colleagues and mentors that have influenced me along the way. I'm sure I will omit people who have made important contributions, but I do not personally know every trace element experimentalist. For anyone who feels slighted, please forgive me.

I have been asked to give some account of what the general culture was like during the walk that I have just described. Nationally, at about that time, there was an OPEC oil embargo, which resulted in long lines at gas stations, and in addition, Iran had taken US Embassy employees as hostages. The Middle East was a tense region, but compared to today, it was rather tame.

Another occurrence during my grad-school internment was that the first two episodes of the Star Wars movies appeared. The second movie, to the best of my recollection, had a showing at Caltech before its general release. I remember standing in line.

In my own case, on a Sunday morning in 1980, one of my housemates/fellow grad-students came running in (he had been at work that Sunday) and announced that there had been a magnitude 6 earthquake at Mammoth Lakes,



CA (Long Valley Caldera). The Caltech Seismo Lab was gearing up to send seismometers to the location. I immediately tried to finagle a way to go along, but I was useless to a seismologist. However, another grad-student, who was going to look for ground breakage to trace the fault, took pity on me and let me tag along. I had never felt an earthquake before.

Because of delays, we did not arrive at Mammoth Lakes until the wee hours of Monday morning. By that time, a second magnitude 6 had occurred and it appeared that my luck for experiencing an earthquake was rapidly running out. But when we stopped to set out our first seismo instrument, the ground was shaking. Just a little, but continuously.

Later on Monday we asked a former Caltech grad-student, who was with the USGS, where it would be interesting to camp. He gave us a location near a Park where little earthquakes were coming so fast and furious that the USGS could only use strong-motion instruments, which filtered out the little stuff. However, we found our way blocked by the authorities. They thought we wanted to use the Park! After some fast talking, we got to where we wanted to go, threw out our sleeping bags, and went to sleep.

But before sleep, it was apparent that our USGS friend had not lied. Every couple of minutes there was a little earthquake, and sometimes you could not even feel them, you would only hear the Sierra Nevada Mountains groan.

At about 7:45 AM Tuesday morning, the third magnitude 6 struck. It started slow as a “thump, thump” and then transitioned into a “THUMP, THUMP.” Landslides came down the mountains, with their associated dust, but we had camped in an area that was totally safe. I had finally experienced a major earthquake, and in a very safe location. ☺

But back to trace element partitioning...

1.2 Definitions

Before going further, it is probably best to first define certain symbols that will be used throughout this paper.

The Nernst partition coefficient D , which is wt. % concentration of element i in one phase normalised to the weight concentration of i in another phase (Nernst, 1891). Typically, the numerator of this quotient will be a solid phase (α) and the denominator will be a liquid phase (β); and the partition coefficient will be given as ${}^iD_{\alpha/\beta}$. There will be instances here when the molar or cation ratio is used rather than the wt. % ratio, but these will be specified. And there will be times when it is convenient to talk in terms of an exchange coefficient $K_D(i/j)_{\alpha/\beta}$, which is the ratio of ${}^iD_{\alpha/\beta}/{}^jD_{\alpha/\beta}$. However, because of the double normalisation, it does not matter how the D 's are expressed with respect to units (*i.e.* molar or wt. %), the K_D value will be the same. And there will be times when the partition coefficient D is more rigorously expressed as an equilibrium constant K for a specific chemical reaction.



These conventions differ from those of Paul Beattie (Beattie *et al.*, 1993), but they are easier to use in a common software application (*e.g.*, Microsoft Word). I believe the most important thing in the Beattie conventions is that a simple partition coefficient is a “D” and that an exchange coefficient is a “K_D”. There are those who still use K_D as a synonym for D, but I do not subscribe to this usage.

There is also the problem of units. I am old enough that I still think in terms of kilocalories (kcal) rather than kilojoules. Mostly I use kcal here. The gas constant R in the calories system is about 2, so converting terms like ΔH/R [equation (1.1)] into a ΔH is trivial in units of calories.

I will pause here to make a personal rant. I hate dealing with pressure units such as Pascals. Any unit that requires 10⁵ of them to comprise a terrestrial atmosphere (one bar) is exceedingly non-geological. Therefore, I will mainly also use bars or kilobars whenever pressure is mentioned. I am not so old-fashioned that I prefer pints, pounds, and horsepower as units, but I do believe that the current usage of unit terminology that has been adopted by our journals is not a step forward, geologically.

1.3 A Simple Equation for D vs. Temperature

The equation that was stuck in my head as I wandered home that evening was:

$$\partial \ln {}^iD / \partial (1/T) = -\Delta H/R \quad (1.1)$$

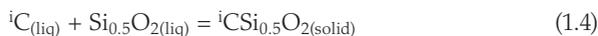
where *i* is the element being partitioned, ΔH is the enthalpy of the partitioning reaction and R is the gas constant. My question was, “What reaction did this ΔH refer to?” The answer may seem obvious, but at the time, it was not obvious to me. One possibility was that the reaction was simply:

$${}^iD = {}^iC_{\text{solid}} / {}^iC_{\text{liquid}} \quad (1.2)$$

but another possibility was that the ΔH pertained to an exchange reaction:

$$K_D(i/j) = {}^iD / {}^jD \quad (1.3)$$

whose temperature dependence would presumably have the same form as equation (1.1). A third possibility was that ΔH referred to a true chemical reaction, where a chemical component was removed from a silicate liquid into a solid. For example, there could be a chemical reaction where a (2+ valence) trace element *i* is partitioned into olivine by a reaction:



In this case, the equilibrium constant K should be substituted for D, and thus:

$$\partial \ln K / \partial (1/T) = -0.5 \Delta H_f / R \quad (1.5)$$

where ΔH_f is the heat of fusion of some pure-olivine component *i*. And since there is a ⁱC on both sides of equation (1.4), it was not clear to me how to distinguish this reaction from equation (1.2). The factor of 0.5 in equation (1.5) merely



denotes that equation (1.4) does not consider that the olivine structure demands two divalent cations, not one.

So my question to myself, wandering home, was what specific ΔH did a plot of $\ln D$ vs. $1/T$ refer to? You may ask why I did not pose this question to my professors. My sense at the time was that they didn't know either, but I could be wrong about that. These were early days in the practice of experimental trace element partitioning.

1.4 Henry's Law

Henry's law, a concept from ancient, 1800's chemistry, obliquely states that it is important for trace elements to be in a concentration regime where the concentration of the trace element in one phase is linearly proportional to the concentration of that element in the other phase. In other words, in that concentration regime, D does not depend on the absolute concentration of the trace element in question, which is an extremely useful concept. Typically, deviations from Henry's law occur at high tracer concentrations. So it is important to be able to measure experimental partition coefficients at low (*i.e.* natural) concentration levels. For many years, this was not really possible.

The standard way of expressing Henry's law thermodynamically is by a slightly different version of the chemical potential equation:

$$\mu_i = \mu^\circ + \ln(\gamma_i x_i) \quad (1.6)$$

where μ is the chemical potential, μ° is the standard state chemical potential of i (which can be measured), and γ is the activity coefficient of component i in the system.

The Henry's law formulation exchanges the μ° term with that of another. Thus, in Henry's law parlance

$$\mu_i = \mu^* + \ln(h_i x_i) \quad (1.7)$$

where h_i is the Henry's law constant. The difference between μ° and μ^* is that μ^* is not a standard state, but a fictitious state that perhaps cannot be measured. It is the value where the Henry's law μ_i vs. $\ln x_i$ intersects the y-axis at $x_i = \text{unity} - i.e.$ the pure component i . This is a useful concept even if the fictitious endmember does not exist. If μ^* is different from μ° , then there is probably a difference in speciation between the Henry's law regime and that of the pure component.

Another aspect of Henry's law is that, within the Henry's law region, the activity of a solute \hat{i} can be expressed as

$$\ln a_i = \ln(h_i x_i) \quad (1.8)$$

where a_i is the chemical activity of some species, h_i is the Henry's law constant, and x_i is the molar concentration of i .



Note that obeying Henry's law does not imply ideality. A low value of h_i indicates that the solvent has a large capacity for i , whereas a large h_i indicates the opposite.

Because the chemical potential of i in the solid and liquid must be equal at equilibrium, D may be written as

$$K h_{i(\text{liq})}/h_{i(\text{sol})} = x_{i(\text{solid})}/x_{i(\text{liquid})} = {}^iD_{\text{sol/liq}} \quad (1.9)$$

where K is the equilibrium constant for equation (1.4), so equation (1.9) is an expression for D at Henry's law concentration levels (Wood and Fraser, 1978). This equation provides a thermodynamic basis for partition coefficients, as long as the concentration of i in both the solid and liquid is within the Henry's law region. This is partly why a high-profile debate over Henry's law (described below) was of such importance to the early trace element community.

As an aside, the original experiments of Henry (1803) also have application to global warming and climate change today. Another aspect of Henry's law is that the solubility of gases in liquids increases with decreasing temperature. So if the Earth's surface temperature should warm (for any reason), the greenhouse gases H_2O and CO_2 should both increase in the Earth's atmosphere, as they evaporate or exsolve from the Earth's oceans.

This same logic also applies to the proposition that ${}^3\text{He}$ may presently be escaping from the Earth's core as it solidifies (e.g., Porcelli and Halliday, 2001). As Hugh O'Neill from the Australian National University (ANU) has pointed out, if the core is cooling, helium should be becoming more soluble, not less, if indeed, Henry's law pertains.



2.1 Percent Level Doping

The timing of my trek home in the dark would have been in the late 1970's, and trace element partitioning had been practised for only a decade, or less. In the late 1960's or early 1970's Mike Drake and Dan Weill at the University of Oregon began doping experiments with rare earth elements (REE) and Sr at wt. % levels (Jones *et al.*, 2015). These concentrations were necessary in order to measure D's using the electron microprobe. Ion probes and laser ablation ICP-MS would only emerge decades later as quantitative instruments. The spatial resolution of the wt. % doping technique was essentially that of the electron microprobe (~2 μm at 15 keV), if the D was not too small. However, if D is very small, then fluorescence of the tracer in nearby glass by x-rays from the crystal can yield a D that is too large.

An issue with the Drake and Weill (1975) experiments was whether wt. % concentrations accurately portrayed the behaviour of trace elements at the ppm level, *i.e.* were they violating Henry's law? But qualitatively at least, these experiments gave clarity to the newly discovered "Eu anomalies" found in lunar rocks. These anomalies express themselves in that the elemental sequence Sm-Eu-Gd is not smooth, but contains a peak or a valley at the position of Eu. Almost all lunar mare basalts had negative Eu anomalies ("valleys") and samples from the anorthositic lunar highlands had complementary positive Eu anomalies ("peaks"; Fig. 2.1).

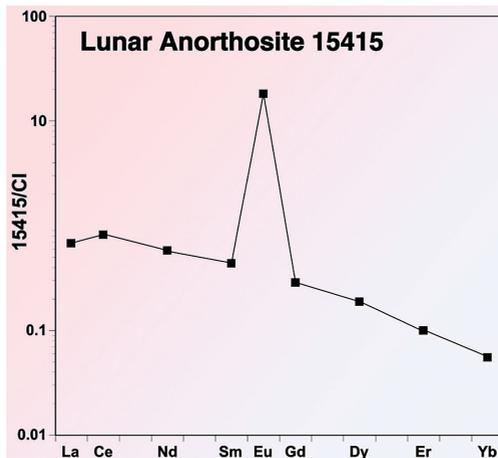


Figure 2.1

Rare earth element pattern of lunar anorthosite 15415, with a prominent, positive Eu anomaly. Data from the Lunar Sample Compendium of Meyer (2011).



These observations were easily explained by the Drake and Weill experiments, which showed that Eu^{2+} , under reducing lunar conditions (*i.e.* low fO_2 – the effective partial pressure of oxygen), had a strong affinity for plagioclase. This discovery has also been taken as strong evidence for a lunar magma ocean – with Eu-enriched plagioclase floating up to the crust, leaving Eu-depleted liquids behind (*e.g.*, Taylor, 1982). This difference in Eu^{2+} and Eu^{3+} geochemistry had not been previously recognised because, on Earth, Eu is dominantly Eu^{3+} , so that Eu anomalies are less common.

2.2 Beta Radiography and Henry's Law

Slightly later, but still in the early- to mid-1970's, a second experimental/analytical technique was developed: beta autoradiography (Mysen and Seitz, 1975). A radioactive tracer, that decayed by beta particle (e^-) emission, was spiked into an experiment, and the quenched, polished, experimental charge was then exposed to a photographic film – a “nuclear emulsion”. The photographic image recorded the distribution of the radioactive tracer, and the “blackness” of the developed emulsion over crystal and glass was then translated into a partition coefficient. This allowed trace element partitioning experiments to be performed at true trace concentrations (10-100 ppm).

Not every beta emitter was a suitable choice for these experiments. Preferably, the radioactive tracer had a low-energy beta and no accompanying gamma ray. The energy of the beta and the presence of gamma rays controlled the spatial resolution of the photographic analytical technique.

At that time, the two most commonly used dopant isotopes were ^{151}Sm and ^{63}Ni , because of (i) their short (but not too short) half-lives; (ii) the low energy of their betas; (iii) their low gamma ray emission; and (iv) their inherent geochemical interest (Mysen, 1976; Carnegie Institution of Washington, Geophysical Laboratory). And although its beta energy was higher (and, therefore, the spatial resolution was not as good), some work was also performed using ^{14}C , another element of geochemical interest (*e.g.*, Tingle, 1987).

At about the same time, there quickly developed two main analytical techniques for measuring D's using beta tracks: (i) the Bjorn Mysen approach of optically counting individual dots (tracks?) on the developed nuclear emulsion (Mysen and Seitz, 1975); and (ii) electron microprobe analysis of the developed emulsion using Ag concentrations to calculate a D (Holloway and Drake, 1977). Mysen's advice to novice beta-track counters was to “*keep your eyeballs steady.*”

Because this new approach allowed experimenters to dope at truly “trace” levels, Henry's law could be investigated in more rigorous detail. Thus, Mysen (1979) found that Ni in olivine diverged from the Henry's law regime at concentrations higher than about 1000 ppm, with ^{63}Ni decreasing at higher concentration levels (Fig. 2.2). However, Drake and Holloway (1981) could not reproduce Mysen's results, and, therefore, comments and replies ensued. Also, Harrison



and Wood (1980; CIW Geophysical Lab) found that Sm and Tm entering garnet deviated from Henry's law below ~10 ppm, with ^{54}SmD and ^{149}TmD increasing as concentrations became lower (Fig. 2.3; Mysen, 1978). Harrison and Wood attributed this to REE entering defect structures, with the Henry's law region being at the higher concentration regime. So Mysen interpreted the Henry's law region for Ni in olivine to be below 1000 ppm, whereas Harrison and Wood interpreted the Henry's law region for REE in garnet to be above 10 ppm. This was somewhat perplexing.

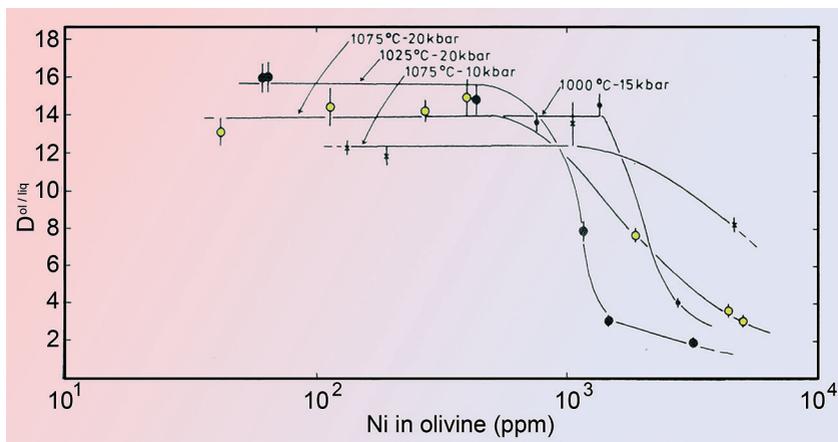


Figure 2.2 $^{54}\text{NiD}_{\text{ol/liq}}$ vs. Ni concentration, modified from Mysen (1978). Beta radiography analyses of Ni partitioning into olivine showed large values below about 1000 ppm and then decreased precipitously at higher Ni concentrations. See text for a discussion of Henry's law implications.

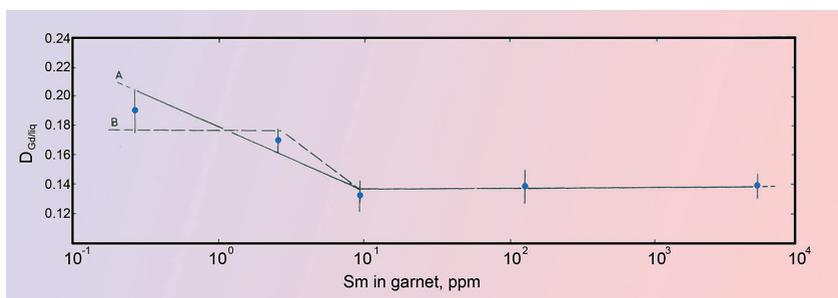


Figure 2.3 $^{54}\text{SmD}_{\text{gnt/liq}}$ vs. Sm concentration, modified from Mysen (1978). Beta radiography analyses of Sm partitioning into garnet showed larger values below about 1 ppm and then decreased at higher Sm concentrations. See text for a discussion of Henry's law implications.



Later, Bruce Watson of Rensselaer Polytechnic Institute (Watson, 1985) noted that, in natural samples, there was really no evidence that Henry's law had been violated. He cited several examples of why violation of Henry's law seemed non-existent. Again, this called the beta-track D's into question.

Additionally, others had noted that the nuclear odd-even effect, which determines the natural abundances of the REE, argued against Henry's law deviations at low concentration levels. Because of nuclear stability issues (*i.e.* the nuclear shell model; *e.g.*, Goepfert-Mayer, 1948), the REE have a "saw-tooth" pattern in terms of their absolute concentrations.

Proton-neutron numbers have been found to be very helpful in determining nuclear stability and, therefore, to understanding chondritic abundances. Even-even (even proton and even neutron) nuclei are more stable than even-odd nuclei, which are more stable than odd-odd nuclei. For example in chondrites, Ce, being an even-even nucleus, is about three times more abundant than La, an even-odd nucleus (*e.g.*, Newsom, 1995), even though they are next to each other in the Periodic Table. But chondrite-normalised REE patterns in igneous rocks are smooth, suggesting that deviation from Henry's law at very low concentration levels is not a real issue.

An argument against this point of view is that individual REE concentrations are not such an issue in natural samples, but rather, it is the sum of individual REE (and Y?) abundances that determines Henry's law REE deviations (Watson, 1985).

2.3 Fission Track Analysis

A third, but less utilised technique was to dope at the ppm level with a fissionable tracer such as ^{235}U or ^{239}Pu . Using this doping technique, the partition coefficient was measured by irradiating the experimental charge with thermal neutrons in a conventional nuclear reactor, using a mica detector to measure the density of the resultant fission fragments over crystal and glass (*e.g.*, Benjamin *et al.*, 1978). The mica was then etched with hydrofluoric acid to reveal the tracks. These could be counted either optically or by SEM imaging. The latter was preferred when track densities were high. This method gave concentration information with a spatial resolution of about $10\ \mu\text{m}$ (Fig. 2.4).



Figure 2.4 Fission track map of Pu partitioning between diopside and liquid (modified from Jones, 1981). Blackest areas signify the highest Pu concentrations (*i.e.* glass). Three pyroxene crystals can be observed. The spatial scale of the largest pyroxene crystal is a few hundred microns. The $^{Pu}D_{\text{pyx/liq}}$ is about 0.17.



2.4 Partitioning Between Immiscible Liquids

Another very influential paper from Bruce Watson also appeared during this time period (Watson, 1976). Watson performed a set of experiments showing how trace elements partitioned between immiscible silicate liquids in the K_2O - FeO - Al_2O_3 - SiO_2 system. This paper gave insights into how liquid composition could affect crystal/liquid partitioning. Watson's initial work was quickly followed up by Ryerson and Hess (1978). Most highly-charged incompatible trace elements, such as the REE, preferred to be in the FeO -rich, de-polymerised, "basaltic" liquid, rather than the polymerised Al_2O_3 - SiO_2 -rich liquid.

2.5 Onuma Diagrams

Onuma *et al.* (1968) were probably the first to point out that, for natural samples, phenocryst-matrix pairs defined regular trends on a $\log D$ vs. ionic radius (r) plot. In particular, a series of iso-valent trace elements could be fitted with a parabola, suggesting an r^2 dependence. So, for a given phenocryst-matrix pair, iso-valent parabolas could be generated from 2+, 3+, and (maybe) 4+ cations. Figure 2.5 shows various valence-state ions partitioning into the Ca site of augite (Onuma *et al.*, 1968). The apices of these parabolas presumably yielded the size of the site that the ion partitioned into and also predicted a maximum D for some perfectly-sized ion of a specific ionic charge.

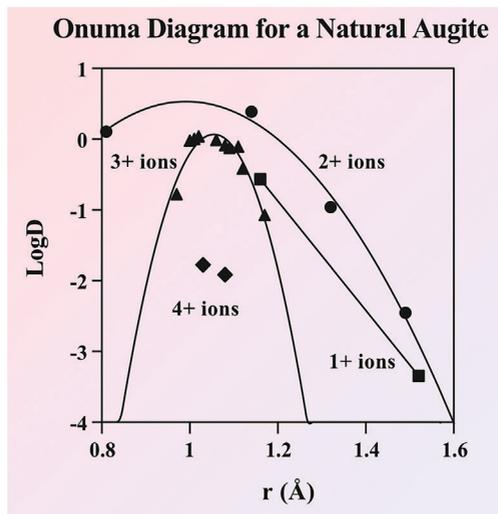


Figure 2.5

Trends of cations partitioning into the Ca site in augite as a function of ionic radius. Data from Onuma *et al.* (1968). Individual iso-valent trends are labelled.



I remember advocating to my apartment-mate (grad-students were poor then, too) that this r^2 dependence could be understood in terms of a Hooke's law (spring constant) formulation where the force F between a trace element ion and the anions surrounding its crystallographic site was given by

$$F = \sum -k\Delta r \quad (2.1)$$

where Δr was the mismatch between an optimal ionic radius r_o for that crystallographic site and the actual radius of the ion r_i , and k is a constant that is proportional to the "strength" of the spring. The \sum represents a summation over all cation-oxygen bonds in a mineralogical site – e.g., in an octahedral site there would be six such Δr 's. An r_i that is either too large or too small with respect to r_o would strain the spring. And the energetic consequences of that would be given by

$$\ln D \sim \Delta E = \int F(\Delta r) d\Delta r = -k \sum \int \Delta r d\Delta r = -k \sum \Delta r^2/2 \quad (2.2)$$

which would explain the observed parabolic nature of the Onuma diagram. I had no clue that a much more elegant stress-strain theory had already been worked out by Brice (1975). The Brice equation is now the basis for the Blundy-Wood model of trace element partitioning (Blundy and Wood, 1994):

$$D = D_o \exp \left\{ (-4p E N/RT) \left[r_o/2 (\Delta r)^2 - 1/3 (\Delta r)^3 \right] \right\} \quad (2.3)$$

where N is Avogadro's Number, E is Young's Modulus, T is temperature in Kelvin, and R is the gas constant. Thus, Onuma diagrams are not really simple functions of Δr^2 but also depend on Δr^3 .

In convincing my fellow grad-student of my over-simplified calculation, I got some quizzing. "Do you mean that an ion that is too small can produce as much strain as an ion that is too big?" And my answer was, "Yes." He seemed satisfied with that. This was gratifying to me, since he was not an easy person to please.

2.6 Crystal Field Effects

The importance of crystal field effects in geological systems was mainly introduced by Roger Burns at the Massachusetts Institute of Technology (MIT; Burns, 1970). Onuma diagrams (Figs. 2.6 and 2.7) show that, for the particularly simple case of olivine/liquid partitioning, some elements deviate appreciably from the values predicted by other cations of the same valence. These deviations are quite clear for Cr, Ni, Zn, and V. For Cr, V, and Ni, the deviations are in the positive direction and are almost certainly caused by crystal field stabilisation energy (CFSE) effects. Cr^{3+} , V^{3+} , and Ni^{2+} have significant CFS energies. Fe^{2+} and Cr^{2+} also have crystal field stabilisations, but are smaller.



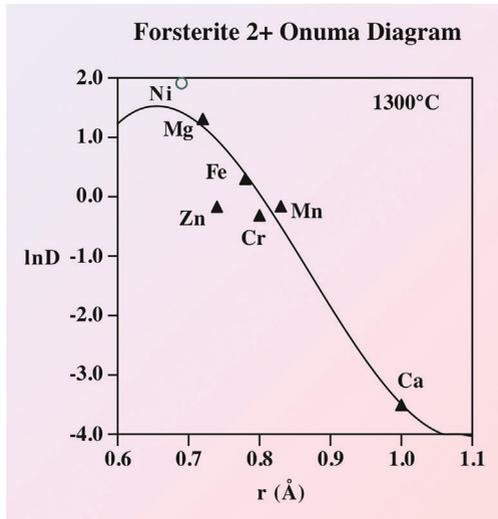


Figure 2.6 Partitioning of 2+ cations into forsterite vs. ionic radius. Data from Hanson (unpublished) and Hanson and Jones (1998). Line is a third-order polynomial fit, omitting Ni and Zn. See text for discussion of Zn and Ni.

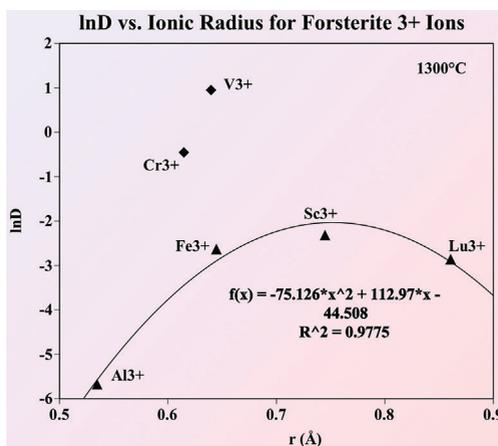


Figure 2.7 Partitioning of 3+ cations into forsterite vs. ionic radius. Data from Hanson (unpublished) and Hanson and Jones (1998). Line is a second-order polynomial fit omitting Cr and V. See text for discussion of Cr and V.



Most discussion of CFSE for Cr, Fe, and Ni has assumed octahedral coordination for these ions. The negative deviation of Zn^{2+} is because Zn^{2+} prefers to be in a tetrahedral coordination (e.g., Greenwood and Earnshaw, 1984); and further, Zn^{2+} has no inherent CFSE. The root cause, however, is the same – crystal field effects.

Figure 2.7 shows the effect of CFSE for V^{3+} and Cr^{3+} , partitioning into forsterite, compared to ions that have either no, or small, CFS energies. Chromium has a $D_{\text{ol/liq}}$ of nearly unity; and vanadium has a $D_{\text{ol/liq}}$ of nearly three. As will be discussed in more detail later, these modestly large D 's can occur even though charge balance is required to satisfy the olivine structure. And in a general way, the compatibilities of Cr and V into forsterite correlate with their theoretical, low-pressure CFSE.

Of course, the more traditional means of accommodating a charge imbalance is by coupled substitution. For example, in diopsidic pyroxenes, the entry of a Na into the lattice can be legitimised by also accepting an Al – both ions entering M sites. But in the case of 3+ ions entering the olivine structure, charge balance is difficult.

Consider the case of a 3+ ion in an olivine M site being charge-compensated by an Al entering a nearby T site. Figure 2.7 indicates that this mechanism is virtually impossible. The partition coefficient for Al into forsterite is so low that it verges on the detection limit of the electron microprobe. Therefore, in the specific case of 3+ ions entering olivine, creation of vacancies seems much more plausible.

But note the interplay between CFSE and Onuma diagrams. Plotting $\log D$ vs. ionic radius makes the relationship between ionic radius and CFSE extremely clear. Without a theoretical underpinning, the data in Figure 2.7 (for example) would appear to be random scatter.

2.7 The 1977 Sedona Conference

Mike Drake and John Holloway organised a conference on experimental trace element partitioning (GCA: June, 1978); and many issues were addressed at that time. Somewhat to Drake's displeasure, I later suggested that this conference nearly killed off the experimental partitioning community (Jones, 1993). For reasons given below, several important issues were addressed, but were not resolved. So, after the conference, I believe many people voted with their feet and left experimental trace element partitioning. I believe they felt that the discipline was too complicated and not well-enough constrained – *i.e.* an immature science. Several issues contributed to this:

Siting of trace elements. My recollection of this conference is that Peter Buseck showed TEM images of silicate crystals rife with defects and emphasised that trace elements need not follow the rules of stoichiometry (Buseck and Veblen,



1978). Elements entering crystals at the ppm level (or worse, at the ppb level) might partition into defects, rather than into well-defined crystallographic sites. This was discouraging.

Non-Henrian behaviour at low concentrations. Wendy Harrison and Bernie Wood showed data indicating that D 's increased at very low tracer concentrations and did not obey Henry's law – *i.e.* D was a function of tracer concentration (Harrison and Wood, 1980). Prior to this, people had assumed that Henry's law was violated only at high concentrations. Wendy and Bernie attributed their results to mineralogical defects, thereby reinforcing Buseck's observations.

The world vs. Mysen (1978). Nobody seemed to agree with Mysen's experiments on Ni partitioning into olivine. In particular, Leeman and Lindstrom (1978) and Drake and Holloway (1981) could not reproduce Mysen's results. Since Mysen had pioneered the beta track analytical technique, this was a cause for concern. Some of these discussions became a little raucous, perhaps fueled by the keg of beer in the back of the room.

The constraints of thermodynamics. There was also an instance where Alex Navrotsky asked a speaker about a thermodynamic constraint and the speaker replied that this was so complicated that it would require much more work. Navrotsky replied that she had performed the calculation during his talk and that she had the result. This was another reminder that trace element partitioning was still an immature discipline.

There is a saying about the 1960's that goes "*if you can remember the '60's, you weren't there.*" To a degree, this also holds for the Sedona Conference. I only remember parts of it.

2.8 An Aside: Graduate School Applications

As an addendum to the '70's, I will mention that I did apply to grad-school in the middle of that decade. My dad initially said "*No*" because he thought he would have to pay for it. He didn't understand that I wasn't asking his permission.

At least at that time, you could send your GRE scores to three schools for free. For various reasons, my three schools were SUNY Stonybrook, Arizona State, and Caltech. And for no really good reason, at some point in the process, I decided that I would much prefer to go west of the Mississippi River.

One day I came home from classes and discovered a telegram at my apartment door. I had never received a telegram before, nor have I since. The telegram informed me that I had been accepted at ASU, and I was "wowed."

A few weeks later I got a letter from Stonybrook, written by Don Lindsley. The letter said that they would like to accept me into their graduate program, but that my application file was incomplete. I needed to send them one more letter of recommendation and an actual application. I had neglected to fill out



an application form. Needless to say, this is one of the better letters I have ever received; but by that time I had already been accepted to a school west of the Mississippi and, therefore, I forgot about this gracious letter.

A few years ago, when I was an Acting Division Chief at the Johnson Space Center (JSC), I saw Lindsley at an AGU meeting and needed to talk to him about a few JSC issues, so I asked if we could do lunch. After our main business was over, I recounted the story about his letter. I knew he wouldn't remember, but I really did wish to thank him. After the tale was over he said, "*That was you?*" Apparently, he did remember that letter; and it wasn't altogether clear that this was a good thing.



3.1 The Influence of Don Burnett

One of those at the Sedona Conference who saw opportunity, rather than insoluble problems, was my thesis advisor, Don Burnett. He recognised that, as yet, there was no rigorous beta-track analytical technique and, being a good nuclear and analytical chemist, he proposed to devise one. Don's view was that the beta-track method had been used, but had never been validated. That became an important part of my Ph.D. thesis (Jones and Burnett, 1981). Don has probably not gotten the credit he deserves for jumping into the trace element partitioning arena.

Don and I made an odd couple. But perhaps that was partially a good thing. The things that I eventually became good at were not really the things Don was good at. Consequently, there was a bit of symbiosis in our relationship. But there were also a number of arguments, especially during my final year. I was anxious to graduate, but Don seemed to not like the direction the thesis was going, so there was tension.

There are moments in everybody's lives that are so engraved in your memory that you remember where you were and what happened as if it were yesterday. One of my vivid moments was when I was walking down California Ave., toward Lake Street, in Pasadena with Burnett. We were heading to lunch. This was about 1976, and I had not yet started doing trace element partitioning. At that time, I was mapping the distribution of U in an LL6 ordinary chondrite, St. Severin, using fission tracks. St. Severin was of some importance because of the amount of work that had already been done on it. It was the type locality for the then currently-accepted value of $^{244}\text{Pu}/^{238}\text{U}$ in the early solar system (~0.015; Podosek, 1970). But Burnett did not buy into the methodology by which this $^{244}\text{Pu}/^{238}\text{U}$ had arisen. In theory, my work should have had some relevance to the Pu/U story, but I was simply interested in where the U was residing and how it partitioned. I wasn't seeing the bigger picture.

At least part of my myopia was because the critical Pu/U measurement for St. Severin had been performed using Xe measurements, *à la* Podosek, and I wasn't measuring Xe. But in front of the Pie and Burger on California Ave., Burnett informed me in no uncertain terms that my task was to use my U analyses to evaluate the correctness of somebody else's Xe analyses. Woah! This was a bit mind-boggling. And it also radically changed my thinking about how science is done and how one does science. I'm a person who sometimes needs to have his pump primed before I really understand certain concepts, and Don primed my pump that day. Eventually, in my thesis, I would recommend a downward revision of the St. Severin $^{244}\text{Pu}/^{238}\text{U}$ ratio by a factor of three.



I should also say that Don later evaluated my experimental results from a very distant viewpoint. He was not in the lab when the experiments were performed. He had never done these kinds of experiments. Yet, he could look at the data and critique my results. This was not altogether different from the discussion in front of the Pie and Burger. Statistical analysis, simple logic, and comparison to previous results could allow you to evaluate data that you had not acquired yourself. That was a lesson that has stood me in good stead.

3.2 What I Really Wanted to do for My Thesis

My eventual thesis consisted of three parts: (i) the distribution of U in a highly-equilibrated ordinary chondrite (Jones and Burnett, 1979); (ii) the development of an analytical technique to quantify the measurement of beta tracks (Jones and Burnett, 1981); and (iii) experimental partitioning of Pu and Sm between diopside and whitlockite (Jones and Burnett, 1987).

But after the chondrite project was over, I wanted to perform partitioning experiments on U and Th and compare their results to a natural sample that had crystallised much more slowly than any laboratory experiments, and Burnett was initially encouraging. To this end, I decided that the best natural sample was a drill core that the USGS had obtained from the Kilauea Makaopuhi lava lake in Hawaii. There was a section of a Makaopuhi core that had coexisting augite and glass, and Burnett and a fellow grad-student, Maritza Stapanian, had developed a fission track technique that could measure both U and Th.

Somehow, I determined that a USGS scientist, Tom Wright, had control of or access to these samples, so I called him up. I introduced myself, told him about my proposed project, and requested a particular sample from a particular drill core. To the best of my recollection, Wright started laughing uncontrollably, but then said something like, “Great!” This took me aback. I didn’t know what to do, and so I had to ask, “Are you being facetious?” He then stopped laughing and said something like, “No, I’ve wanted somebody to do this for years!” And he then sent me a few grams of sample.

I do not remember the Stapanian-Burnett technique in detail, but it required special preparations. A thin sample slice had to be epoxied to an aluminum cylinder and then bombarded with deuterons (I think) at an accelerator. The Al backing was to conduct away heat, as I recall. So only after I had prepared several Makaopuhi samples in this way, Burnett told me that he would not support the project. I had let Tom Wright down, and I regret that.

With hindsight, I acknowledge that my proposal was not a very exciting thesis topic. The comparison between experiment and Kilauea could have been fundamental, but I doubt that my results would ever have been accepted by *Science* or *Nature*. On the other hand, my actual thesis results would probably not have been accepted by *Science* or *Nature* either.



3.3 Clair Patterson

The Caltech system was such that a grad-student had two advisors (at least it was in my time): an academic advisor and a thesis advisor. In theory, the academic advisor was there to make sure that you were proceeding nicely towards graduation: taking the right courses and checking the right boxes. And Clair Patterson was my academic advisor. I have no idea how this came about, but Patterson was perhaps the worst possible choice for this role. He had no interest in me, but I would routinely ask him to sign off on my class-work choices every term. And he would routinely sign.

My recollection is that, on our first meeting, he asked if I had done my undergrad work at Washington University (St. Louis) – probably because my thesis advisor, Burnett, had close ties there. But, no, I had been an undergrad at the University of Kentucky. His response was, “Well, maybe that’s far enough north that you know some math.”

Patterson was probably a genius, and he certainly figures into my maxim that “genius is best admired from afar.” Pat was not a Caltech professor, at least not while I was there. But the anecdotal story was that every once in a while, he would demand to be made a professor. And then, after some faculty grumbling and after a professorial offer was made, he would turn it down. I believe he also had his office sound-proofed to the extent that he had a false floor installed above the actual floor to dampen sound from below. I don’t recall there being anything particularly noisy on the floor beneath his office. His office may have been over the geology library.

Patterson merely had two important scientific accomplishments: he was the first person to accurately measure the age of the Earth (*e.g.*, Patterson, 1956), and he was, perhaps more than anyone else, responsible for removing leaded gasoline from American gas stations. Either of these could constitute a normal scientist’s life’s work. The last decades of his career were spent documenting the extent of anthropogenic heavy metal pollution (*e.g.*, Ng and Patterson, 1982; Davidson, 1998).

He agreed to be the chairman of my Ph.D. thesis defense, but only after I persuaded him that it really was a thesis defense. He initially thought that I was taking my candidacy exams for the n-th time, and he wanted no part of that.

Pat was not very predictable. Well into my fifth year, I asked him to sign my class-work card once again, which by then was mainly devoted to research. I had been admitted to candidacy, which meant that I had completed all required coursework. But suddenly, he sat me down and wanted to know if I had taken enough physical chemistry (P-chem). This was a little unnerving (even though I knew I didn’t need more coursework to graduate), because I still needed him to sign that card.



So I told him that I had taken three P-chem courses as an undergrad. That didn't cut the mustard. What had I taken at Caltech? Nowhere else mattered. Well, I had taken "Introduction to the Chemical Bond" in the chemistry department. OK, what else? Uggh. Well, I had taken Thermodynamics I & II from Hugh Taylor and Gerry Wasserburg. Suddenly, everything was OK, and he signed my card. *"That's better than anything you'll get in Chemistry."* I had been saved from a Patterson attempt at being conscientious.

Pat did have a wry sense of humour. One of the funniest encounters that I've ever seen was between Pat and Dorothy (Dotty) Woolum (a Burnett collaborator). Pat came across Dotty one day as she was entering the building, burdened with files, books, purses, and whatever – as per usual. At that time Dotty smoked, and Pat asked her for a light (of a cigarette). Dotty started shifting all of her stuff to get at her cigarette lighter for about 5 seconds before she stopped, grinned, and said, *"Pat, you don't smoke!"* Pat just smiled and ambled away.

One of my standard questions to young scientists is, *"When did we first know the age of the Earth?"* And for extra credit, who was responsible? Except for those who are already geochronologists, they never know when nor whom. Sad.

3.4 Combined Beta Radiography and Fission-Track Analyses

Following on the work of Holloway and Drake (1977), I began using SEM/EDS analyses of Ag in nuclear emulsions to determine ^{Sm}D for diopside ($CaMgSi_2O_6$) and whitlockite [$Ca_3(PO_4)_2$] using experiments doped with ^{151}Sm .

Without going into details, this turned out to be fruitful. There were many complexities involved with using nuclear emulsions as beta detectors, but it eventually appeared that these were mostly tractable (Jones and Burnett, 1981). From an analytical precision point-of-view, it turned out that the Mysen (1976) partition coefficients were given analytical errors that were much too small. Mysen counted individual "tracks" and these N tracks gave one-sigma (Poisson) counting statistics of $(N)^{0.5}/N$, so that counting 100 "tracks" presumably gave counting statistics of $\pm 10\%$. But a time-series of exposed nuclear emulsions, analysed using the SEM technique, indicated that each beta particle produced about ten "tracks." Therefore, counting 100 "tracks" yielded a precision of about 30%, not 10%. Burnett's vision that Ag radiography could be quantified proved to be correct – or at least correct enough. This helped to explain the difference in $^{Ni}D_{ol/liq}$ measurements between Mysen and other experimenters. Mysen's analytical precision was simply much poorer than he had thought.

There was also the issue of the range of the beta particles. Crystals needed to be several times larger than the distance that was required to stop all betas entering from the surrounding glass, in order to obtain a meaningful D – especially if the D was $\ll 1$. For ^{151}Sm analyses, crystals needed to be rather greater than 40 μm , if D was small.



I also analysed plutonium in the same ^{151}Sm -doped charges by counting fission tracks, again using an SEM. The experiments were irradiated with thermal neutrons at a local (UCLA) reactor. By that time, track counting (using mica detectors) was an established technique, so no analytical development was necessary. Still, because neutron irradiation produces other radioactive species, the Pu analyses could not be performed until it was clear that the Sm partition coefficients needed no further refining. Only then could the experimental charges be safely neutron-irradiated.

The combination of these two analytical techniques allowed us to compare the geochemistry of an actinide to that of a lanthanide in the same experiment; and the general geochemical behaviour of lanthanides was much better understood. An important take-home message was that the ability to measure D 's for multiple elements in the same experimental charge (and at the same spatial location) is a great force multiplier. The innovation of trace-level doping and LA-ICPMS measurements has greatly reinforced this concept.

3.5 Some Minor Lab Issues

Although Burnett was my thesis advisor, the person who taught me to perform experiments was a fellow grad-student, Tim Benjamin. Tim was only one year ahead of me, but he had set up Burnett's experimental lab. He had a pre-doctoral fellowship at the CIW Geophysical Lab, and so he spent about half of each year there. Tim had also visited Dan Weill's lab at the University of Oregon. When Tim was at the Geophysical Lab, he did piston-cylinder experiments, and when he was at Caltech he performed one bar experiments. So Burnett's basic experimental regime was modelled after those at Oregon and the Geophysical Lab. Tim and I got along pretty well, and I learned a lot from him. For example, he once taught me how to deal with a particular faculty member: insult him before he has the chance to insult you. Get in the first punch. Coming from a rural, southern environment where these things were not done, I had to adapt somewhat.

In the late '70's there came a time when we needed to make a new starting composition. Partly, our old starting compositions were becoming used up; plus, it was time to start doping with radioactive Sm. This also gave us the chance to correct a problem with earlier starting compositions.

Our earlier spikes for the actinides had come from Oak Ridge in the form of HCl solutions. A consequence of this was that there was ubiquitous Cl contamination. A further consequence was that we would grow chlorapatites $[\text{Ca}_5(\text{PO}_4)_3\text{Cl}]$ when whitlockite $[\text{Ca}_3(\text{PO}_4)_2]$ was the desired phosphate phase. Whitlockites would eventually grow, but only after most of the Cl had been sequestered into apatite.

When we began thinking about new compositions, I remembered from my freshman chemistry class that all nitrate salts are soluble (Sorum, 1967), and it seemed just as easy to order the spikes in nitric acid solutions. We did that, and then the Cl problem was behind us. The nitrogen just boiled away.



But during that process, I needed to spike, melt, and re-grind this new starting composition. I remember coming in on a Saturday to quench this new composition. Instead, I discovered that the experiment had quenched itself. The Pt wire that I had used to suspend the starting composition (contained in a sealed Pt tube) had not been strong enough to bear the weight of the tube at high temperature. The charge had dropped, the tube had ruptured, and the spiked silicate liquid had leaked out. And I had to call Burnett on a weekend and tell him. ☹

You just haven't lived until you've had a few grams of Pu-spiked liquid leak all over your furnace. But we eventually recovered from that debacle, and I learned a few things in the process. Subsequent checking of the lab by radiation safety showed that the leak had been contained within the furnace. Plutonium and samarium really are refractory elements.

3.6 Mike Drake

In 1980, Mike Drake, at the University of Arizona in Tucson (UA), advertised for a post-doc. Even then, I was savvy enough to know that people might tell you things on the phone that they would not put into writing. Therefore, I phoned Drake, expressed my interest in the job, and bluntly asked if a candidate had already been chosen. Drake responded that no candidate had been chosen and that he would welcome my application. So I applied.

My ambition at the time was that, if I couldn't get an academic position, I wanted to post-doc at a place that would improve my knowledge about the origin of basalt. My petrology background was very spotty. At that time, Caltech was not known for its igneous petrology.

Drake had done a lot of work related to lunar and meteoritic basalts, so I judged this to be a good opportunity for me. And somewhere, deep in my heart of hearts, I knew that I was not yet ready to be an academic professor. With hindsight, I believe this was correct.

At that same time, I did apply for a faculty job at UC Davis and got an interview at a Fall AGU. My recollection is that the interviewer was a palaeontologist. After I described my thesis work, he said that he would describe me to his faculty as a theorist. I remonstrated that I was an experimentalist. He then changed his evaluation to 90 % theory and 10 % experimental.

I did get the job with Drake, and the result was a long and fruitful symbiosis. Drake had a reputation for being a very demanding person, so I viewed my new job with some measure of trepidation. But since it was the only offer I had, I gladly took it. In actuality, it was a much less stressful environment than I had been accustomed to. And over time, Drake and I became more like friends, as opposed to having a hierarchal boss-employee type of relationship. Considering that we were both rather strong-willed individuals, I look back and think that the number of times we truly aggravated each other was surprisingly few (at least on my side of the equation).



After grad-school, I needed some time to decompress. Therefore, Mike's philosophy of work hard and play hard was perfect for me at that snapshot in time. I look back on my time in Tucson as both rewarding and pivotal. I miss Mike Drake.

3.7 A Letter of Reference

For various reasons, I lived in fear of the day when I would have to venture out into the real world and need a letter of recommendation from Don Burnett. And fear is not too strong a word. But I did get the job with Drake and, therefore, Burnett must have written an acceptable letter.

Some years later, after Drake and I had become better acquainted, I told him the story (probably over a beer) of how I had dreaded that Burnett letter. In his best English professorial style, Drake explained to me that he could not allow me to see a letter written in confidence. However, he believed that he could give me a synopsis of the Burnett letter that would not violate any confidentiality rules:

“(i) Jones is not a very good student; (ii) he's not a very good researcher; (iii) he will probably never make any important scientific contributions; but (iv) he's probably better than anyone on your faculty.”

When I left UA to go to JSC, Mike decided that the statute of limitations had been exceeded and that if I wanted to see Burnett's letter, I could. I declined, believing that it would just raise my blood pressure. In rebuttal, Burnett admits to only (i) and (iv).

3.8 Looking for a Real Job

I do not remember the exact timing, but probably while I was at UA, I applied for a faculty job at Northwestern University. Later, I received a letter from the Department Chair (?) thanking me for my application. He said that they had narrowed the candidates down to a short list and unfortunately, “your name was not on that list”. I confess that I'm hard put to come up with a more insulting rejection letter that does not involve obscenities. The fact that I remember this letter (and its author) decades later serves my point.

It was also during that time period when I would have an occasional lunch with two of my UA post-doc colleagues, Allan Treiman and Dave Wark, an Australian who is now deceased.

Allan and I would talk about jobs that we had applied to (or not applied to). Dave would then ask where we learned about these jobs. We would point out the weekly/monthly job ads in *EOS* and *Geotimes*. And I know that, on at least one occasion after that, Dave again asked about how we found out about these jobs. My suspicion is that Dave was simply waiting for someone to call him up and offer him a job.



Also about that time, Bill McKinnon (Wash. U., St. Louis) and I placed a job-wanted ad in *EOS*. The ad was mostly written by Bill, who is rather better-trained in the classics than I am. We advertised ourselves as Philosopher Kings who were applying for “hereditary positions of power and influence.” But mysteriously, no job offers arose from this advertisement. Apparently, Philosopher Kings were not in great demand at the time.

However, one reply was very interesting. A grad-student from Lamont-Doherty (Columbia University) sought a job from us, if we ever managed to achieve our kingdoms. She aspired to be a vassal, and she thought her grad-school experience made her extremely qualified for that position. She said that she had taken advanced courses in “contrition and shit-eating,” and that she had minored in obsequiousness. I sincerely regret that we never had a job to offer her.

A few years later, on a visit to Lamont, I told someone the story of this “vassal application” and asked if this lady was still around. I did not even vaguely remember her name. Apparently that did not matter; people seemed to automatically know who I was talking about. The answer was, “*No, she went to Scripps.*”



4. TUCSON DAYS: PART I (MOSTLY SILICATE)

4.1 An Excursion into Metal Partitioning

My first post-doctoral task was an experimental partitioning study of Ge between solid and liquid metal in the Fe-Ni system. Drake hired me to measure one particular partition coefficient ${}^{\text{Ge}}D_{\text{sol met/liq met}}$. In those days, a single D at a single (T-P) condition was considered publishable, but Drake had somewhat despaired of getting reliable experimental results in metallic systems. I was the third post-doc assigned to this task. So Mike promised me that, if I could get a decent value for ${}^{\text{Ge}}D$, he would ditch this project and we would go on to better, more profitable things. The value of ${}^{\text{Ge}}D$ was important because Ge plays a large role in the classification of iron meteorites (e.g., Wasson, 1967; Scott, 1972).

4.2 A Personal Note

This was a problematic time for me, and so I put aside my interest in the theory of silicate trace element partitioning. I had not actually finished my Ph.D. when I went to work for Drake, and therefore, I spent the first three months both in Drake's lab doing ${}^{\text{Ge}}D_{\text{sol met/liq met}}$ experiments and driving back and forth to Pasadena, CA, to finish writing and defending my thesis. Tucson and Pasadena are about 750 km apart. Mike insisted that my Ph.D. defense come first, which immediately defined him to me as a good guy.

To compound the problem, Drake was not in Tucson. Mike was on sabbatical in Cambridge (UK), so I really had no one to seriously talk to about my continual experimental problems.

On one of these trips from Tucson to Pasadena the transmission of my car failed; fortunately, it failed after I got to Pasadena, rather than in the Mohave Desert between Phoenix and Palm Springs. I managed to coast into the street of the grad-student house where I would be staying. But, eventually, the Ge partitioning experiments worked. I will revisit them below.

4.3 Olivine/Liquid Partition Coefficients (Part I)

After the metal partitioning experiments began to work, I returned, in my "copious spare time" (a Drake group catch-phrase), to olivine/liquid partitioning. This seemed to be the simplest system to investigate, and on weekends, I plotted various literature D 's vs. various parameters and got nowhere. But, finally, I came across a paper by Hart and Davis (1978) on ${}^{\text{Ni}}D_{\text{ol/liq}}$ that captured my attention. These authors plotted ${}^{\text{Ni}}D_{\text{ol/liq}}$ vs. $1/\text{MgO}_{\text{liq}}$ for a haplobasaltic (*i.e.* FeO-free) system and found a linear dependence. This suggested to me that, because Hart



and Davis had experimented in an FeO-free system, plots of $^{Ni}D_{ol/liq}$ vs. $^{Mg}D_{ol/liq}$ might be useful. In an FeO-free system, $1/MgO_{liq}$ is analogous to $^{Mg}D_{ol/liq}$, on a cation basis. And although my recollection is that my inspiration came from Hart and Davis, Watson (1977) had earlier used the same $D_{ol/liq}$ vs. $1/MgO_{liq}$ for $^{Mn}D_{ol/liq}$ and I certainly knew about his paper.

Immediately, using this formulation, linear trends appeared for ^{Fe}D , ^{Mn}D , and ^{Ni}D when regressed vs. ^{Mg}D – all in cation units (Fig. 4.1). Charlie Langmuir (then at SUNY Stony Brook) had done similar regressions for major elements (Langmuir and Hanson, 1981), where stoichiometry and mass balance determined mineral compositions. But in my formulation, Mn and Ni partitioning were modelled rather well, and mass-balance relationships did not pertain. Mn and Ni are negligible in terms of a typical olivine mass balance.

I published these results (Jones, 1984a), and in that paper, I also attempted a thermodynamic interpretation of their meaning. The thermodynamic analysis was totally wrong. A reviewer tried to point this out to me, but did not explain why it was wrong. I saw nothing amiss and told the editor so. About six months after the paper was published, simply glancing at the paper, I saw my mistake. My derivation had started with

$$D = A/T + B \quad (4.1)$$

But I *should* have started with

$$\ln D = A/T + B \quad (4.2)$$

the integral equivalent of equation (1.1)

$$\partial \ln D / \partial (1/T) = -\Delta H/R \quad (4.3)$$

I had had a blind spot, so I derived an equation that gave me an answer I liked, but the derivation was badly wrong. The physical interpretation, though, was essentially correct. Still, it is good to be cautious of calculations that give the desired answer.

Despite my derivation, there was an important point to this paper that has perhaps been somewhat overlooked. Because there is a linear equation relating $^{Fe}D_{ol/liq}$ to $^{Mg}D_{ol/liq}$ and because Fe and Mg totally dominate all other 2+ cations in typical olivines, mass balance allows the prediction of ^{Fe}D , ^{Mn}D , and ^{Ni}D , if the composition of the basaltic liquid is known, because $^{Mg}D_{ol/liq}$ or $^{Mg}D_{opx/liq}$ can be calculated:

$$^{Mg}D_{\text{mafic solid/liq}} = (F - B \text{FeO}X_{liq}) / (A \text{FeO}X_{liq} + \text{MgO}X_{liq}) \quad (4.4)$$

where F is 0.667 for olivine and 0.5 for pyroxene (*i.e.* octahedral site fraction of cations), and the A and B parameters in Tables 4.1 and 4.2 are those from Jones (1995). Therefore, when $^{Mg}D_{\text{mafic solid/liq}}$ is calculated, other partition coefficients can then be calculated as well. Typical values of $^{Mg}D_{\text{mafic solid/liq}}$ are given in Table 4.3 (Jones, 1995).



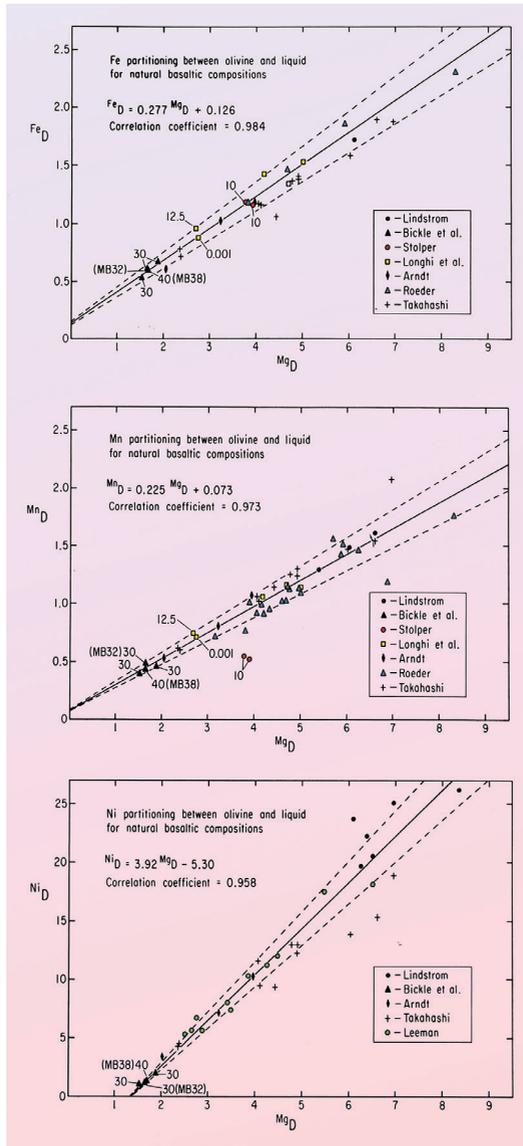


Figure 4.1

Fe, Ni, $MnD_{ol/liq}$ vs. $MgD_{ol/liq}$ (modified from Jones, 1984a). Many of the non-ideal terms appear to cancel on plots such as these. Also, the trends on individual plots appear to be independent of temperature and pressure. Numbers associated with individual data points refer to the pressure of the experiment.



Table 4.1 Regression parameters for molar olivine/liquid partition coefficients.

$D_i = A D_{MgO} + B$					
Element	A	B	Number of Experiments	Correlation Coefficient r	σD_i^s
FeO [#]	0.298	0.027	898	0.93	0.13
Mn	0.259	0.049	204	0.91	0.23
Ni	3.346	3.665	148	0.92	2.0
Co	0.786	0.385	68	0.96	0.23
Sc	0.063	0.034	11	0.88	0.02
Mg	1.00	0.00	898	—	0.168

[#] Corrected for Fe₂O₃ in the liquid. ^sStandard error.

Table 4.2 Regression parameters for molar subcalcic pyroxene partition coefficients.

$D_i = A D_{MgO} + B$					
Element	A	B	Number of Experiments	Correlation Coefficient r	σD_i^s
FeO [#]	0.129	0.264	146	0.91	0.26
Mn	0.352	0.025	108	0.91	0.24
Ni	1.206	0.263	10	0.87	0.239
Co	0.467	0.14	7	0.98	0.02
Sc	0.522	-0.66	8	0.95	0.16
Mg	1.00	0.00	167	—	0.154

[#] Corrected for Fe₂O₃ in the liquid. ^sStandard error.

Table 4.3 Typical DMgO values for planetary basalts.

D_{MgO}^*	Komatiite [#]	Alkali Olivine Basalt	MORB [#]	Andesite	Lunar Mare Basalt	Eucrite	Shergottite [#]
Olivine	1.8	4.2	4.8	8.4	2.6	4.6	3.8
Orthopyroxene	1.3	3.2	3.3	6.6	2.0	3.8	2.9

[#] Fe₂O₃ taken to be 10 % of FeO total.



Equation (4.4) does not predict whether olivine or low-Ca pyroxene is stable, but if either is on the liquidus, then the D 's for Mg, Fe, Mn, and Ni can all be calculated. This was later expanded to some other elements, and also refined in several ways (Jones, 1986, 1988; Beattie *et al.*, 1991; Hanson and Jones, 1998; Musselwhite *et al.*, 2006; Filiberto and Dasgupta, 2011).

I used these olivine/liquid relationships and other considerations to calculate the composition of the Eucrite Parent Body (Jones, 1984b). Eucrites are basaltic (tholiitic), achondritic meteorites that probably (mostly) originate from the asteroid 4-Vesta (*e.g.*, Consolmagno and Drake, 1977). Trace-, minor-, and major-element modelling all seemed to yield the same answer: Main Group Eucrites were produced by 20–30 % partial melting that left little or no pyroxene behind in the residuum. This creates a currently unresolved problem because there is another suite of meteorites, the diogenites (magnesian pyroxenites), that are also believed to be derived from 4-Vesta. Therefore, how to relate the eucrites to the diogenites in a simple igneous process is currently unknown – at least to me (Hoff *et al.*, 2014), although I will concede that some magma ocean models come close (Righter and Drake, 1997a; Mandler and Elkins-Tanton, 2013).

These D relationships were also part of a project with John Delano to estimate a bulk composition for the Moon (Jones and Delano, 1989). Delano had derived a two-component model for the Moon's composition using primitive, ultramafic lunar glasses. Delano's thinking had internalised Norman Bowen's principle that glasses are more important than rocks to igneous petrology, because it could not be doubted that an igneous glass was a true liquid composition. Because of the vagaries of rock-forming processes, the same cannot necessarily be said of a basalt, and even less so of a gabbro. My contribution was to turn John Delano's concept into a three-component model, which, theoretically at least, should be more general. We envisioned a model with three components: (i) a solid residuum from an early melting event; (ii) cumulates from that early melting event; and (iii) a residual liquid that had just begun to crystallise plagioclase. In the simplest case of equilibrium crystallisation, the solution was analytical and was in the form of the quadratic equation:

$$X_{\text{cumulus-materials from the magma ocean}} = [-b \pm (b^2 - 4ac)^{0.5}]/(2a) \quad (4.5)$$

and this result then allowed us to calculate $X_{\text{olivine residuum}}$ and $X_{\text{residual liquid}}$. Our bulk lunar silicate results agreed rather well with those of Ringwood *et al.* (1987), but disagreed with the more widely-accepted result of Taylor (1982).

Our partial melting residuum was specifically chosen to provide a high-Mg# source for the lunar Mg-suite. But at that time, it was not universally recognised that the Mg-suite had a KREEP characteristic (*e.g.*, Meyer *et al.*, 1971). The co-mingling of high-Mg# mafics (Fo_{90}) with a highly-evolved KREEP signature still remains an issue in lunar petrology.

My recollection is that this manuscript with Delano must have been the most-reviewed paper ever (probably not true). For several reasons, this paper went through about three review cycles and two associate editors; and it became exhausting. Perseverance is sometimes a virtue.



Another result of the Delano collaboration was that we found that the real difference between the Ringwood and Taylor lunar compositions derived from their individual assumptions about the lunar Mg/Si ratio. Ringwood favoured a terrestrial Mg/Si ratio for the Moon, whereas Taylor preferred the chondritic (CI) value. Mike Drake once assigned our paper as required reading to a graduate seminar that he taught with Jay Melosh. He thought that any paper that could relate the Ringwood and Taylor models was worth his students' attention.

4.4 Olivine/Liquid Partition Coefficients (Part II)

It took me quite a while to realise that a paper published in the proceedings of the Sedona Conference gave me the answer to the question on my late night trek home (Leeman and Lindstrom, 1978). These authors plotted $\ln "D" vs. 1/T$ for olivine/liquid in four different ways:

- (i) $\ln \text{NiD}(\text{wt. \%})_{\text{ol/liq}} vs. 1/T$
- (ii) $\ln \text{NiD}(\text{molar})_{\text{ol/liq}} vs. 1/T$
- (iii) $\ln K_{\text{Ni-olivine}} vs. 1/T$ where K is the equilibrium constant for equation (1.4)
- (iv) $\ln K_{\text{D}}(\text{Ni/Mg})_{\text{ol/liq}} vs. 1/T$

What I had not noticed was that methods (i), (ii), and (iii) all gave the same value of ΔH (*i.e.* slope of the $1/T$ regression; Fig. 4.2; Table 4.4). This meant that the ΔH of all three plots yielded the heat of formation of a Ni-olivine component

Table 4.4 Equilibrium constants for reactions i-iv above (after Leeman and Lindstrom, 1978).

No.	Data set regressed	n ^a	K _i		K _{ii}		K _{iii}		K _{iv}	
			A ^b	B	A	B	A	B	A	B
1	Natural basalt compositions	14	12242 ± 492	-5.55 ± 0.32	12913 ± 533	-6.10 ± 0.34	12753 ± 509	-5.20 ± 0.33	4396 ± 560	-1.94 ± 0.36
2	Combine 1 with synthetic compositions	29	12564 ± 970	-5.79 ± 0.62	13512 ± 754	-6.46 ± 0.48	13211 ± 717	-5.50 ± 0.46	4741 ± 1198	-2.24 ± 0.77
3	Combine 2 with compositions of Hart <i>et al.</i> (1976) with Si/O < 0.30	34	12842 ± 748	-5.97 ± 0.48	13599 ± 608	-6.51 ± 0.39	12826 ± 590	-5.24 ± 0.38	4400 ± 775	-2.02 ± 0.49
4	Combine 3 with compositions of Bird (1971)	38	13376 ± 726	-6.34 ± 0.46	14298 ± 679	-6.99 ± 0.43	13452 ± 673	-5.67 ± 0.43	4475 ± 656	-2.07 ± 0.42

^a n = number of experimental data points used in the regression analysis; in most cases each such data point is an average for several separate runs made at the same temperature.

^b A and B are regression parameters for the equation: $\ln K = \frac{A}{T} + B$.



from a silicate liquid, *i.e.* methods (i) and (ii) agreed with method (iii). In a world where olivine and liquid were both thermodynamically ideal solutions, the ΔH from these plots would yield the heat of fusion (ΔH_f) of $\text{NiSi}_{0.5}\text{O}_2$ olivine. In reality, the Leeman and Lindstrom (1978) ΔH 's only give an approximate value for the ΔH_f of Ni-olivine. Still, olivine solid solutions (and the liquid solutions from which magnesian olivine crystallises) are often rather ideal, unless the system is very rich in alkalis.

Equation (1.4) also requires that the K of equation (1.5) depends on the silica activity of the liquid. Leeman and Lindstrom (1978) assumed that $2 \times \text{Si/O}$ for their silicate liquids approximated the silica activity of the silicate liquid. A pure SiO_2 liquid has a Si/O of 0.5, so a multiplication factor of two leads to an activity of one.

I once mentioned to an esteemed colleague that, if both the solid and liquid were totally ideal, trace element partitioning between them would still have a temperature dependence. This is because of the influence of ΔH_f via equation (1.1). I recall that this colleague then looked at me as though I were a two-headed calf.

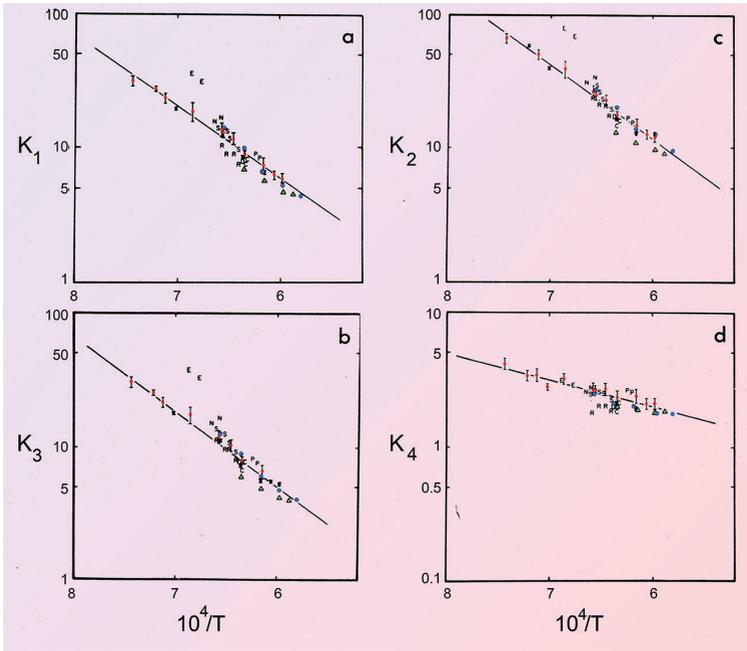


Figure 4.2

Various formulations of $\text{Ni}^{D_{\text{ol/liq}}}$ vs. $1/T$ (modified from Leeman and Lindstrom, 1978). **(a)** Weight percent D. **(b)** Molar percent D. **(c)** Equilibrium constant (K) for the formation of Ni-olivine from the silicate liquid. **(d)** Exchange reaction K_D for Ni and Mg between olivine and liquid. The main outliers in these diagrams are haplo-basalt (*i.e.* FeO-free) compositions E and N, which were both alkali rich. K_1 through K_4 correspond to the K_i through K_{iv} of Table 4.4.



Leeman and Lindstrom's method (iv) yielded a much shallower slope than the other three plots. This suggested that the temperature dependence of $K_D(\text{Ni}/\text{Mg})_{\text{ol/liq}}$ was linked to the differences in ΔH_f between forsterite and Ni-olivine.

The Leeman and Lindstrom experiments also addressed the issue of Henry's law. Plotting ${}^{\text{Ni}}D_{\text{ol/liq}}$ vs. ${}^{\text{Mg}}D_{\text{ol/liq}}$, it became apparent that the data became non-linear when the mole fraction of Ni approached ~0.15. For crystal-chemical reasons, Ni prefers the M1 olivine site (Galoisy *et al.*, 1995). Therefore, deviations from Henry's law began to occur when Ni filled approximately half of the M1 sites. Fe^{2+} also prefers the M1 site, so there is competition between Fe and Ni, if Ni abundances become too high. So there was still no reason to believe that Ni in the ~thousand-ppm range should deviate from Henry's law *à la* Mysen (1979).

4.5 Olivine/Liquid Partition Coefficients (Part III): Quickly "Apparating¹" to the Future

Rather than proceed in strict chronological order, it seems better to fast-forward, continuing on the theme of olivine-liquid partitioning.

4.5.1 The thermodynamics of D vs. D diagrams

The derivation of a thermodynamic analysis for the linear D vs. D diagrams in Jones (1984a) was quite a failure. A second try much later was perhaps better, but not sufficiently better so as to publish. Under the persistent prodding of Allan Treiman (LPI), I made a third attempt that I believe was successful (Jones, 2010). The linear relationship between both ${}^{\text{Fe}}D$ vs. ${}^{\text{Mg}}D$ and ${}^{\text{Mn}}D$ vs. ${}^{\text{Mg}}D$ is explicable by the observation that $K_D(\text{Fe}/\text{Mg})$ and $K_D(\text{Mn}/\text{Mg})$ are both rather constant (*i.e.* both D vs. D regressions pass close to the origin). The real issue was how to deal with ${}^{\text{Ni}}D$ vs. ${}^{\text{Mg}}D$, which definitely does not pass close to the origin and which predicts that ${}^{\text{Ni}}D_{\text{ol/liq}}$ might become <1 (*i.e.* incompatible) under some conditions. In other words, $K_D(\text{Ni}/\text{Mg})$ cannot be considered constant.

But even here, refinement through iteration seems to justify the conclusion that the ${}^{\text{Ni}}D$ vs. ${}^{\text{Mg}}D$ slope is simply attributable to difference in heats of fusion. Under the assumption that at least a portion of ${}^{\text{Ni}}D_{\text{ol/liq}}$ vs. ${}^{\text{Mg}}D_{\text{ol/liq}}$ space is linear, *i.e.*

$${}^{\text{Ni}}D_{\text{ol/liq}} = a {}^{\text{Mg}}D_{\text{ol/liq}} + b \quad (4.6)$$

$K_D(\text{Ni}/\text{Mg})$ can be modelled as

$$K_D(\text{Ni}/\text{Mg}) = a + b/{}^{\text{Mg}}D_{\text{ol/liq}} \quad (4.7)$$

by dividing both sides of equation (4.6) by ${}^{\text{Mg}}D_{\text{ol/liq}}$. More minor mathematical fiddling yields the result:

$${}^{\text{Ni}}D = \{a ({}^{\text{Mg}}D^{-1}) + b \ln {}^{\text{Mg}}D\} \Delta H_f(\text{Ni})/\Delta H_f(\text{Mg}) \quad (4.8)$$

where the ratio of the heats of fusion provide a link between ${}^{\text{Ni}}D$ and ${}^{\text{Mg}}D$.

1. <http://harrypotter.wikia.com/wiki/Apparition>



However, even though this equation was able to fit the data of Leeman and Lindstrom (1978) (which deviate from linearity at high values of ^{Mg}D), it appears that this is an unnecessary refinement. Modern data from Claude Herzberg (pers. comm.; Herzberg *et al.*, 2013) do not show the non-linear ^{Ni}D vs. ^{Mg}D trend seen in the Leeman and Lindstrom (1978) data set. A likely explanation for the difference between the two data sets is analytical uncertainty (Longhi, pers. comm.). Modern electron microprobe and ion microprobe techniques are better equipped to deal with low abundances of Ni in the silicate liquid at high ^{Mg}D .

4.5.2 Beattie refinements

Paul Beattie improved on my method in several ways (Beattie *et al.*, 1991). He added more data, expanded the elements that were modelled, and used the f_{O_2} parameterisation of Kilinc *et al.* (1983) to correct for the presence of Fe^{3+} . I do not agree with all of Paul's regressions. For example, I think that his parameterisation of ^{Ca}D may not stand the test of time. [For example, $^{Ca}D_{ol/liq}$ in silica-undersaturated systems can be quite different from those of normal basalts (Jurewicz *et al.*, 1993a)]. However, he was more rigorous than I had been about f_{O_2} . The regressions tables A1 and A2 for olivine and orthopyroxene are taken from Paul's paper.

4.5.3 Mg# refinements

Justin Filiberto (Southern Illinois University), Don Musselwhite (LPI), Allan Treiman (LPI), and Rajdeep Dasgupta (Rice University) have shown that planetary basalts with lower Mg#'s (*i.e.* extra-terrestrial basalts) have a small, but significant increase in $K_D(Fe/Mg)_{ol/liq}$ of ~20 % (*e.g.*, Musselwhite *et al.*, 2006; Filiberto and Dasgupta, 2011). Experiments in FeO-rich systems with ~18-20 wt. % FeO have $K_D(Fe/Mg)_{ol/liq}$ of ~0.35, as opposed to the Roeder and Emslie (1970) terrestrial value of ~0.3. Regardless, it is difficult to top Roeder and Emslie's succinct title ("Olivine-liquid equilibrium").

It is not totally clear whether the difference in K_D between terrestrial and planetary olivines is intrinsically due to Mg# or whether terrestrial K_D 's are lower because the higher terrestrial f_{O_2} increases the abundance of Fe^{3+} . Ostensibly, using the Beattie *et al.* (1991)/Jones (1995) regressions, the presence of Fe^{3+} has been accounted for; although there could be higher order terms not considered by the Kilinc *et al.* (1983) or the Kress and Carmichael (1991) methods. But, on balance, it is most likely that the change in K_D is intrinsic to Mg#.

4.5.4 Effect of pressure

The original Jones (1984a) paper included a few high-pressure experiments; and a subsequent Jones (1988) abstract on the influence of TiO_2 on $K_D(Fe/Mg)$ showed little, if any, influence of pressure. Another Jones (1986) abstract used



experiments from Takahashi (1986) to argue that the Jones (1984a) olivine ^{Fe}D vs. ^{Mg}D regression held to pressures up to 140 kbar – essentially over the whole olivine stability field. But these data did not really address the issue of whether ^{Ni}D and other trace element regressions are applicable over that pressure range.

4.5.5 Effect of TiO_2

An outgrowth of my collaboration with Delano was that I began trying to understand why experiments on high-Ti lunar mare basalts gave low olivine/liquid values of $K_D(Fe/Mg)$. By that time, I had a ^{Fe}D vs. ^{Mg}D correlation (Jones, 1984a), so it was rather natural to explore areas of composition space where my parameterisation did not work well.

A multivariate regression of the relevant literature experiments indicated that pressure was not a major player, but that the liquid concentrations of FeO, MgO, and TiO_2 were very important. Much subsequent fiddling resulted in an equation that appeared to capture the essence of the experimental results. The hypothesis became that the Jones (1984a) parameterisation could be modified to include TiO_2 by simply assuming that Ti formed a “ferropseudobrookite”, $FeTi_2O_5$, species, in the silicate melt (Jones, 1988). The assumption was that this strong complexation effectively removed FeO from the population of ions that partitioned into olivine, thereby lowering the $K_D(Fe/Mg)$. The equation that best fit the data became

$$K_D(Fe/Mg) = K_D(\text{low-Ti}) ((X_{Fe} - X_{Ti}/2)/X_{Fe}) \quad (4.9)$$

where X_i refers to the ion fraction of i in the silicate liquid and the $K_D(\text{low-Ti})$ is the value predicted by the Jones (1984a) equation. This equation fit the then-existing data with an r value of 0.91.

4.5.6 The incompatibility of compatible elements

Almost all the above discussion has presumed that trace elements are incompatible. This *ain't necessarily so* (Gershwin and Gershwin, 1935) – Ni being a good example. But the thermodynamics of equation (1.1) still hold, so that, as temperature decreases, a compatible element should become more compatible, just as an incompatible element does.

There are two interesting corollaries to this observation. One is that, with decreasing temperature, an incompatible element may eventually become compatible. And this may have importance for crystal/melt partitioning near the solidus or in granitic systems. The second, which is rarely considered, is that with *increasing* temperature, a compatible element may become incompatible. Both possibilities are allowed under equation (1.1).

Longhi *et al.* (2010) suggested that some peculiar features of Ni and Co in lunar basalts could be explained if some of their source regions had formed under conditions where Ni was incompatible in olivine. In particular, they used



my 1984 paper and the Beattie *et al.* (1991) paper to support this view. They also carried out high-temperature experiments in an effort to measure a $^{Ni}D_{ol/liq}$ that was <1 . This they were unable to do, but they did measure a $^{Ni}D_{ol/liq}$ as low as 1.4 at 18 kbar and 1760 °C. Further, their experimental results agreed well with the Beattie *et al.* (1991) $^{Ni}D_{ol/liq}$ vs. $^{Mg}D_{ol/liq}$ correlation.

Elardo *et al.* (2011) followed up on Longhi's suggestion and performed experiments on two bulk silicate Moon compositions. These authors measured $^{Ni}D_{ol/liq} < 1$ in three different experiments, with the lowest being 0.33. And, again, their results mainly agreed with the predictions of Beattie.

Watson (1977) also showed that $^{Mn}D_{ol/liq}$ could, based on composition/temperature, be both compatible and incompatible (Watson's Fig. 5). Even though $^{Ni}D_{ol/liq}$ is perhaps more petrologically interesting, $^{Mn}D_{ol/liq}$ nicely illustrates the point that equation (1.1) explicitly makes.

One difference between the Longhi and Elardo experiments is that Elardo analysed using the ion probe, where detection limits should not be an issue. I remember a distressing summer when a visiting professor came to JSC and measured 200 ppm Ni in a Marjalahti olivine standard that could not have had more than about 20 ppm Ni. And this was using a Cameca SX-100 electron probe, which was state-of-the-art at the time. The reason for this rather high blank level for Ni could never be determined, but Ni analyses in electron probes can be difficult (Capobianco and Amelin, 1994).

And, as noted above, Herzberg *et al.* (2013) also used the Jones-Beattie parameterisation method for $^{Ni}D_{ol/liq}$ to make some important inferences about the origin of some oceanic basalts. And, according to Claude, he and his co-authors had to make very strong arguments to his editors for the Jones-Beattie parameterisation over other competing models. It is always gratifying to see your results used and appreciated.

4.6 Toward a World-View of Trace Element Partitioning in Igneous Silicate Systems

What was not known at the time of the Sedona Conference (but probably should have been guessed) is that, as a general rule, incompatible trace element D's should all increase with decreasing temperature. This could have been predicted from equation (1.1). The convention is that exothermic reactions have a negative ΔH , and almost all solidification reactions are exothermic. So this means that increasing temperature should cause D to decrease and that decreasing temperature should cause D to increase. There may be unusual situations where this simple rule does not hold (there always are), but they cannot be very common. In general, if D appears to be decreasing with decreasing temperature, it probably means that: (i) the experiments are bad, (ii) the analyses are bad, or (iii) both. In



the case of the Drake and Weil (1975) experiments on plagioclase, the apparent increase in some $^{REE3+}D_{\text{plag/liq}}$ with increasing temperature was probably due to the relatively poor analytical capabilities of the time.

4.6.1 Thermodynamics of solidification

A good rule of thumb is that the energy liberated, when a mole of an element solidifies, is $\sim 4 \pm 1$ kcal (~ 16 kJ). Metals such as iron have heats of fusion in this general range. But silicates are not metals; there is no such thing as an atom of olivine. So for the example of Ni-olivine, we must take seven atoms/ions from the silicate liquid to make a molecule of MgNiSiO_4 . This translates into ~ 30 kcal/mole; and the measured heat of fusion of pure Ni_2SiO_4 is even greater – 53 kcal/mole (Sugawara and Akaogi, 2003). If the solid were a calcic pyroxene, $\text{CaNiSi}_2\text{O}_6$, we might expect the heat of fusion to be even somewhat larger, perhaps ~ 40 kcal/mole, because it has ten atoms/ions.

The difference between the pseudo-theoretical Ni-olivine calculation and the measured ΔH_f of Sugawara and Akaogi (2003) is presumably due to crystal field stabilisation energy (CFSE) effects. When Ni enters the olivine structure, it not only releases a nominal heat of fusion, but it also becomes more energetically stable because of crystal field effects (Burns, 1970). And, of course, pure Ni-olivine is different than Ni partitioning into magnesian olivine. More on this below.

Further, if the solid phase is relatively pure and the liquid is not too non-ideal, we might expect plots of $\ln D$ vs. $1/T$ for a major element to approximately yield the heat of fusion of the host phase. In the case of Ni partitioning into olivine, we should hope that a plot of $\ln^{Mg}D_{\text{ol/liq}}$ vs. $1/T$ for those experiments would give the approximate heat of fusion of $\text{MgSi}_{0.5}\text{O}_2$. Thus, plots such as these are useful for evaluating experiments and experimental data. This is one of the lessons learned from the Leeman and Lindstrom (1978) paper.

4.6.2 Phase diagram analogues to incompatible trace element partitioning

A graphical means of illustrating some of these points is to consider a binary T-X eutectic system where the solid has limited solid solution with X (Fig. 4.3). The liquidus curve is approximately defined by the freezing-point equation

$$RT \ln (^iX_{\text{liq}}/^iX_{\text{sol}}) = -\Delta H(i)_{\text{liq/sol}} + T\Delta S(i)_{\text{liq/sol}} \quad (4.10)$$

whose second derivative $\partial^2 T/\partial X^2$ is negative (convex). But the line denoting the extent of solid solution (think of the albite-anorthite or the forsterite-fayalite binary solidus) has a second derivative that is positive (concave).

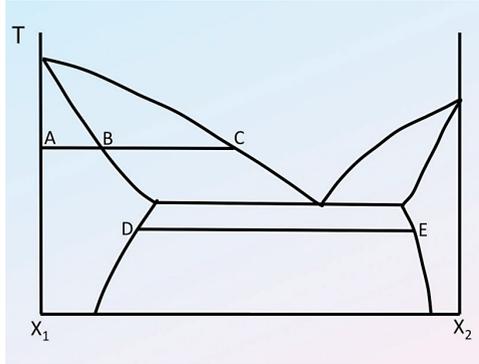
The consequence of this is that the liquidus curve increases in X_2 more slowly than does the solid solution boundary – *i.e.* the two curves get proportionally closer with decreasing T. An isothermal line B-C between these two boundaries can be envisioned as a $^X D$, where



$$X_D = (B - A) / (C - A) = B/C \quad (4.11)$$

And in this case, where X_2 is an incompatible component ($X_D < 1$), X_D will continually increase with decreasing temperature until the solidus is reached.

Figure 4.3 A binary two-component eutectic system with limited solid solution. The isothermal points A, B, and C mark the limits of the second, limited-solid-solution component, X_2 . The partition coefficient of X_2 can be described as $(B-A)/(C-A)$, or B/C . Below the eutectic temperature, the partitioning is controlled by the entropy of mixing, e.g., line D-E.



A tantalising, natural verification of this last observation came from Mahood and Hildreth (1983). These authors noted that mafic minerals in high-silica rhyolites had rather large values of ^{REE}D , just as the theory predicts. But it appears that the Mahood and Hildreth observation was compromised by the presence of REE-rich inclusions in the mafic minerals they had analysed as bulk mineral separates (Michael, 1988). Michael's electron microprobe results reinforce the observation that good spatial resolution is important when analysing for trace elements.

A specific example of the importance of heats of fusion comes from the anorthite-albite system. At high CaO contents, Na partitioning into anorthite is not unlike that of an incompatible trace element partitioning into some host phase. And after quite a bit of thermodynamics, McSween *et al.* (2003) show that the concentration of the albite component in anorthite can be given by

$${}^{Ab}X_{\text{anorthite}} = \{1 - \exp[\Delta H(\text{An})_{\text{liq/sol}}/(R(1/T - 1/T_{\text{An}}))]\} / \{\exp[\Delta H(\text{Ab})_{\text{liq/sol}}/(R(1/T - 1/T_{\text{Ab}}))] - \exp[\Delta H(\text{Ab})_{\text{liq/sol}}/(R(1/T - 1/T_{\text{An}}))]\} \quad (4.12)$$

The important point here is that the anorthite-albite phase diagram can be rather successfully modelled by simply knowing the melting points of anorthite and albite, T_{An} and T_{Ab} , and their heats of fusion, $\Delta H(\text{An})_{\text{liq/sol}}$ and $\Delta H(\text{Ab})_{\text{liq/sol}}$.

4.6.3 Heats of reaction vs. heats of fusion

Even though the above discussions have continually referred to ΔH as a heat of fusion for the sake of simplicity, this is technically incorrect. ΔH 's can only be heats of fusion if the system consists of just one component. An example



would be liquid Ni-olivine crystallising to stoichiometric solid Ni-olivine. In this special case:

$$\Delta H = \Delta H_{\text{fus}} = \Delta S_{\text{fus}}/T \quad (4.13)$$

But, for example, in the case of Ni-olivine crystallising from a Fo-An-Ab liquid:

$$\Delta H = \Delta H_{\text{ideal}} + \Delta H_{\text{nonideal}} = \Delta H_{\text{fus}} + \Delta H_{\text{mix}} \quad (4.14)$$

Without going into detail, the heat of mixing term can incorporate many components. However, I will argue below that, for most silicates, the heat of fusion term is much greater than the heat of mixing term. And note that, by definition, there are no ideal heats of mixing.

4.6.4 Heats-of-mixing in silicate liquids

Navrotsky *et al.* (1980) have given a detailed study of the heats-of-mixing in the diopside-anorthite-albite system, which is interesting in regard to the thermodynamic aspects of partitioning that we are considering here.

Figure 4.4 shows contours of liquid heats-of-mixing within the Di-An-Ab ternary. For the most part, the non-ideal contribution to the partitioning process is only a few kcal/mole. This is of a very different magnitude from the heats-of-fusion

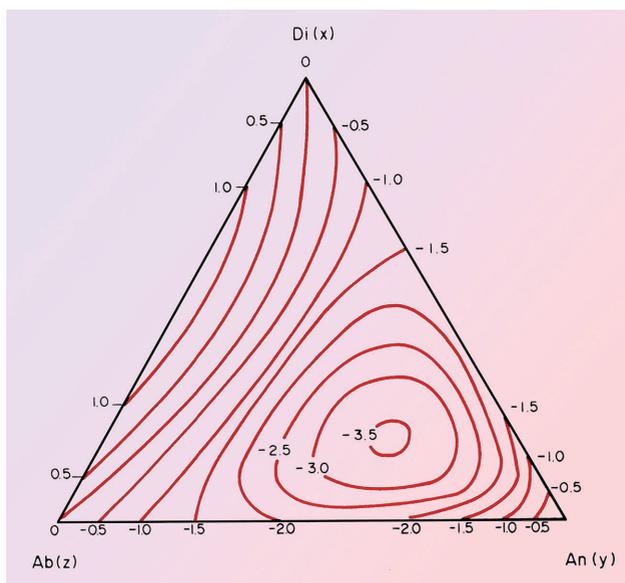


Figure 4.4 Contoured heats of mixing in Diopside-Anorthite-Albite system glasses (modified from Navrotsky *et al.*, 1980). Note that heats of mixing are never more than a few kilocalories per mole.



reported for minerals crystallising from this ternary system (15-35 kcal/mole). Therefore, at igneous temperatures we expect ideal, as opposed to non-ideal, thermodynamics to dominate. This greatly simplifies how the thermodynamics of trace element partitioning should be perceived.

4.6.5 Entropy of mixing at infinite dilution

Even in ideal systems, the entropy of mixing approaches infinity as the concentration of a solute x approaches zero:

$$\Delta S_{\text{mix}} = -R[x \ln x + (1-x) \ln (1-x)] \quad (4.15)$$

As x approaches zero, $(1-x)$ will approach unity, $\ln (1-x)$ will approach zero, and $\ln x$ will approach minus infinity faster than x approaches zero (L'Hopital's Rule), making ΔS_{mix} extremely positive. Therefore, because of the entropy of mixing, there's a little bit of everything in everything.

4.6.6 Condensation from the solar nebula

The foregoing has emphasised the importance of the heat of fusion to trace element partitioning. However, still keeping equation (1.1) in mind, heats of condensation (or sublimation) must, by necessity, be much larger than heats of fusion.

In the case of forsterite olivine, the heat of fusion is about 30 kcal/mole. As an approximation, a change of 50 °C will result in a factor of two change in a D . However, its heat of sublimation/condensation is about 130 kcal/mole (*e.g.*, Nagahara *et al.*, 1994). Therefore, equation (1.1) predicts that the temperature dependence of forsterite condensation from a gas will be much greater than that of forsterite crystallisation from a liquid.

4.6.7 Jones and Burnett (1987)

Several of the issues discussed above were addressed in the Jones and Burnett (1987) paper that finally presented the experimental results of my thesis and also put them into the same sort of thermodynamic construct that I had been using for olivine/liquid partitioning. But here, the main subject was diopside/liquid partitioning, which is rather more complex than olivine partitioning (*e.g.*, Gaetani and Grove, 1995). Although I took a long time to publish, the paper was probably the better for it. I caution, though, that this is not something I would normally recommend for an early-career scientist.

Whether anybody read this paper is a completely different issue. I suspect that many people saw the word plutonium in the title and spent their reading time elsewhere.



Summarising our technique, our $^{5m}D_{\text{diopside/liq}}$ experiments were carried out in the Di-An-Ab system at one bar, between 1300 and 1200 °C. Our dopants were radioactive ^{151}Sm at the ~50 ppm level and ^{239}Pu at the ~10 ppm level.

Henry's law. Serendipitously, two other groups had also performed one bar $^{5m}D_{\text{diopside/liq}}$ experiments in the Di-An-Ab system. Grutzeck *et al.* (1974) and Ray *et al.* (1983) had performed similar experiments, but used Sm doping levels that were different from ours, which were ~50 ppm. Grutzeck *et al.* (1974) used traditional, percent-level doping and analysed their experiments using the electron microprobe; and Ray used an intermediate doping level (~800 ppm) and analysed his experiments using an ion probe. Therefore, it seemed natural to compare the results of these three data sets with respect to Henry's law.

Table 4.5 compares two twin sets of experiments that have similar liquid compositions, but some minor corrections were made to the data before their incorporation into Table 4.5. The first comparison is between our average $^{5m}D_{\text{diopside/liq}}$ and that of the Ray *et al.* (1983) Composition C. This comparison required both a minor fractional crystallisation correction (because the two sets of experiments were not performed at exactly the same temperature) and a modest analytical correction to the Ray *et al.* (1983) analysis because of the lack of a suitable ion probe standard (Ray *et al.*, 1983; Appendix I). The second comparison was between the Ray *et al.* (1983) Composition B and the Grutzeck *et al.* (1974) Composition B. Again, an analytical correction was applied to the Ray data; the Grutzeck data were corrected for a small temperature difference and a small amount of fractional crystallisation.

Table 4.5 Comparison of DI-AN-AB system $^{5m}D_{\text{(diopside/liquid)}}$ among different laboratories.

	Jones & Burnett (1987)	Ray <i>et al.</i> (1983) Comp. C	Ray <i>et al.</i> (1983) Comp. B	Grutzeck <i>et al.</i> (1974) Comp. B
^{5m}D	0.31 ± 0.03 *	0.31 ± 0.03 **	0.41 ± 0.04 *	0.43 ± 0.17 ***
	comparable liquid compositions		comparable liquid compositions	

* Corrected for 20 % fractional crystallisation.

** Corrected for 30 % systematic error (Ray *et al.*, 1983) and 20 % fractional crystallisation.

*** Corrected for 10 % fractional crystallisation and 15 °C temperature difference.

But with these minor caveats, three sets of experiments with three very different doping levels appear to agree very well. This was extremely gratifying. And although others have found Henry's law complications in plagioclase partitioning (*e.g.*, Bindeman and Davis, 2000), I believe percent level doping is well within the Henry's law region for most elements and minerals. But because of the advent of quantitative ion probe and laser-ablation inductively-coupled plasma mass spectrometer (LA-ICPMS) analytical techniques, experimenters with access to these instruments need not rely on my confidence in percent-level doping.



Heats of formation. Figure 4.5 plots $\ln S^m D$ vs. $1/T$ for the data of Ray *et al.* (1983). Three bulk compositions are represented and each composition has D's measured at three different temperatures over a $\sim 100^\circ\text{C}$ range. The temperatures for the three compositional data sets are much the same. Lines through these three "liquid lines of descent" are sub-parallel and all correspond to a ΔH_{fus} of ~ 60 kcal/mole (*i.e.* a fictitious heat of fusion). This reinforces my earlier contention that heats of fusion are large and dominate the partitioning process.

Conversely, the relatively small vertical dispersion in the measured D's at a given temperature is a measure of the effect of composition on partitioning. Over a $\sim 100^\circ\text{C}$ temperature range, the inferred ΔH due to compositional non-ideality in the liquid is on the order of 2-3 kcal/mole. This is very consistent with Figure 4.4 (Navrotsky *et al.*, 1980).

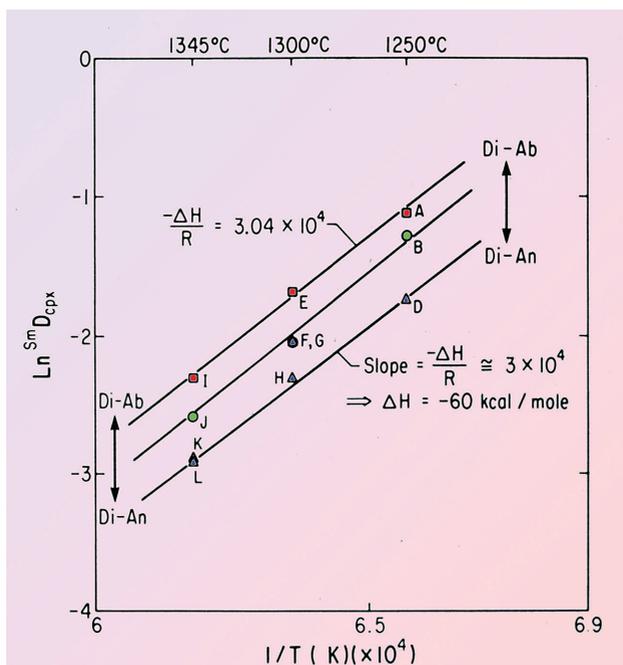


Figure 4.5

$\ln S^m D_{\text{cpx/liq}}$ vs. $1/T(\text{K})$. Three sets of isothermal experiments from Ray *et al.* (1983). Horizontal dispersion for a constant composition with respect to $1/T$ yields a heat of formation of ~ 60 kcal/mole. Vertical dispersion at a constant temperature, but variable composition, gives a measure of the thermodynamics of the compositional dependence, $\sim 2\text{-}3$ kcal/mole.

Further, even non-idealities in the solid are typically small relative to heats of fusion. For example, in the diopside-enstatite system, the solvus between these two pyroxene components may be approximated by a Hildebrand regular



solution (*i.e.* symmetric) interaction parameter W of ~ 6 kcal/mole (*e.g.*, Holland *et al.*, 1979). And because the ΔH_{excess} is proportional to WX^2 , the actual excess ΔH is even smaller, as long as the mole fraction X is less than unity (*i.e.* the system isn't pure). This essentially holds true even though the Di-En solvus is actually asymmetric. Therefore, even the familiar, strong deviation from ideality in the pyroxene system is energetically unimportant compared to heats of fusion. Therefore, I argue that for most high-temperature silicates, the ideal term in equation (4.14) is much more important than the non-ideal term.

But, returning to heats of fusion (*i.e.* formation), the ΔH that we deduce from Figure 4.5 of -60 kcal/mole is not only large, it is overly large. If, instead, we calculate a $\ln K$, assuming ideality in the liquid, the Ray *et al.* (1983) data yield a slightly lower ΔH of -50 kcal/mole. Unfortunately, the heat of fusion of Sm-diopside is unknown, so these estimates cannot be compared to known values.

But Navrotsky *et al.* (1980) have estimated the heat of fusion of diopside to be -30 to -35 kcal/mole, and we can use different melt speciation models to compare the Navrotsky *et al.* result to the Ray *et al.* (1983) data. Without going into details, an ideal melt model gives a ΔH_f of diopside of about -60 kcal/mole, in agreement with the $^{\text{Sm}}\text{D}$ data – but not in such good agreement with Navrotsky *et al.* (1980). However, a Nielsen and Drake (1979) melt model (a modified Bottinga and Weill (1972) model) yielded a ΔH_f for diopside of ~ -40 kcal/mole. Although not perfect, this model worked much better than the others Burnett and I tested. And, as noted earlier, the simple rule-of-thumb of -4 kcal/atom would predict a ΔH_{fus} for diopside of about -40 kcal/mole.

So for our purposes here, it appears that using more realistic $\ln K$ *vs.* $1/T$ calculations gives more reasonable heats of formation than the simpler, easier $\ln D$ *vs.* $1/T$ regressions. Regardless, all these predict large >30 kcal/mole heats of fusion for calcic pyroxenes and their components.

4.7 Subsolidus Partitioning

The binary, limited-solid-solution diagram (Fig. 4.3) also illustrates why it can be dangerous to estimate igneous partition coefficients using subsolidus assemblages. Below the solidus of a binary system, partitioning of the incompatible component X is no longer determined by a heat of fusion. Instead, partitioning is now controlled by the entropy of mixing between two components separated by a solvus (*e.g.*, line D-E, Fig. 4.3).

Phinney and Morrison (1990) and Treiman (1996) have both pointed out the unreliability of using metamorphic assemblages and igneous D 's to reconstruct precursor igneous trace element compositions and patterns. Heats of fusion dominate the thermodynamics of igneous partitioning. Mixing thermodynamics dominate subsolidus partitioning. Igneous D 's should not be applied to metamorphic assemblages, and *vice versa*.



A corollary of Figure 4.3 is that the maximum solubility of an incompatible element in its host mineral occurs near the solidus. In Figure 4.3 the solubility of the incompatible element in its host phase increases until the eutectic temperature is reached and then decreases thereafter.

A likely natural example of this is the Angra dos Reis meteorite (Jones, 1981). Angra dos Reis (AdoR) is an augite (fassaitic) cumulate that has been metamorphosed to such a degree that igneous zoning has been erased (Prinz *et al.*, 1977). Fission track analysis of uranium in AdoR pyroxenes gives U concentrations of about 200 ppb (Bhandari *et al.*, 1971). This is approximately 20x CI and rivals that of whitlockite phosphates in ordinary chondrites. And because these analyses were performed using fission tracks, there is little doubt that the U actually resided in the pyroxene. Therefore, it appears that this U incorporation into pyroxene occurred at a temperature near the solidus of the AdoR parent liquid. A trapped liquid within the cumulate was likely incorporated into the fassaitic pyroxene during a subsolidus high-temperature metamorphic event. Otherwise, if AdoR fassaites reflect the U concentration of their parent liquid, then the U content of that liquid was extreme (Jones, 1981).

Another possibility is that fassaitic pyroxene, with high concentrations of charge-balancing cations such as Al and Ti, might substantially boost the compatibility of elements such as U and REE. However, McKay *et al.* (1988) found only marginal differences in $^{REE}D_{ca-pyx/liq}$ between fassaites and diopsides (*cf.*, McKay *et al.* (1988) and Grutzeck *et al.* (1974)). This suggests that enhanced ^{U}D by charge balance is not the solution to the AdoR pyroxene U concentrations. Near-solidus assimilation of residual liquid into the fassaite seems more probable to me.

4.8 A Short Critique of Traditional Petrologic Thermodynamics

For better or for worse, the 1950's thermodynamic revolution in the petrology community was largely led by metamorphic petrologists such as J.B. Thompson (Harvard University) and H.P. Eugster (Johns Hopkins University). Non-geologic materials scientists were also involved in this process. And although these individuals were also interested in high-temperature igneous petrology, much of their influence concentrated on subsolidus metamorphic issues.

As noted above, the thermodynamics of igneous and metamorphic equilibria are quite different. But, because of historical underpinnings, the concerns of metamorphic petrologists have been imprinted on igneous petrology to a great degree.

Reiterating, the heats of fusion that so dominate igneous processes are in the realm of tens of kcal per mole. Conversely, enthalpies of reaction that are important to metamorphic processes may be only a few kcal per mole. Consequently, in low-temperature metamorphic experiments, it is important to use experiments of long duration and to “reverse” those experiments to make sure that there has not been a metastable excursion from true equilibrium. Reversal



experiments require coming to the desired experimental state from at least two different conditions. These conditions may require changes in pressure, temperature, bulk composition, or oxygen fugacity. But the hope is that a convergence from different intensive variable directions (*i.e.* T, P, X, f_{O_2}) will lead to a consistent result.

For example, it would be important to constrain the quartz-fayalite-iron oxygen buffer by both lowering the f_{O_2} of a quartz-fayalite assemblage until metallic iron appeared and then reversing that reaction by increasing the f_{O_2} of a quartz-iron assemblage until fayalite appeared. At low temperatures, both kinetic and nucleation issues may lead to confusing and conflicting results, especially when heats of reaction are small.

A good friend and colleague of mine is a great believer in reversal experiments in high-temperature igneous systems. Personally, I am not. My observation is that my friend's reversal experiments seldom, if ever, contradict his original experiment. Therefore, I think these reversal experiments are not actually testing what he believes they're testing. Kinetics at high temperature are such that, if a crystal nucleates and homogenises, there is little reason to suspect phase disequilibrium. This crystal may represent a metastable equilibrium, but probably not disequilibrium. However, at low, metamorphic temperatures, reversals are both evil and necessary. I will confess, however, that my lack of confidence in high-temperature reversals may not be justified if the sample was held at a temperature too high above the liquidus for too long. The combined effects of these processes seem to destroy those regions of short-range order that were destined to become the nuclei crystals (more on this below).

Another concern, considering the rather sluggish diffusivities of most elements in silicate minerals, is whether true reversals in trace element partitioning are generally physically possible. There are at least two ways of confronting this issue:

- (i) For his thesis work on Eu partitioning, Mike Drake observed that the compositional variation in plagioclase decreased as the duration of the experiment increased. Since diffusive equilibration was hardly possible, some have speculated that this approach to equilibrium occurred by crystal dissolution and reprecipitation (Ostwald ripening). This could be a kinder, gentler means of growing crystals than simply taking an experimental charge to a desired run temperature.
- (ii) If diffusive equilibration for crystals is impossibly slow on a laboratory timescale, crystal growth essentially proceeds by fractional crystallisation, not equilibrium crystallisation. Consequently, the experimental crystals will be zoned and cannot be subsequently equilibrated. But at low degrees of crystallisation it is difficult to distinguish between equilibrium and fractional crystallisation. Therefore, Gordon McKay always advocated keeping the degree of crystallisation small ($\sim <10\%$).



5.1 Partitioning in the Fe-Ni-X(Tracer) System

After I had been a post-doc at UA for a couple of years, Mike Drake gave me a document, produced by my post-doc predecessor, Dave (Duck) Mittlefehldt (JSC), entitled, “Advice to the Unwary.” This turn-up documented all of Duck’s troubles in doing solid metal/liquid metal partitioning in the Fe-Ni-X system. I also had had a lot of problems with these experiments, but none of my issues overlapped with Duck’s! No overlap on a Venn diagram. We invented our experimental troubles independently. With hindsight, these experiments were not hard. They were actually easy, but that ease came only after learning some experimental pitfalls.

As noted above, my task was to measure a reliable value for $^{68}\text{Ge}_{\text{sol met/liquid met}}$. For the first couple of months, none of my germanium partitioning experiments worked. In Mike’s sabbatical absence, my supervisor was Laurel Wilkening, so one day I went to her office to cry on her shoulder. Laurel was not an experimentalist, but she was comforting. She observed that, as an experimentalist, I must be used to long durations where experiments didn’t work. My short answer was “No.” For my thesis, I had essentially been handed an experimental recipe that needed no particular innovation. Of course, not all of my thesis experiments worked, but there had never been a multi-month drought.

My current problem was that all of my experimental charges were either totally solid or totally liquid at the time of the quench. But this was not necessarily unexpected. The two-phase field for Fe-Ni metal solid-liquid equilibrium has a very narrow temperature range, and nobody really knew how adding germanium would affect the Fe-Ni phase diagram. Because of these concerns, Drake suggested that I run four experiments at a time, each with a different Fe/Ni ratio, hoping that at least one charge would land inside the solidus-liquidus loop. I think I inherited that experimental rationale from Duck. In desperation, and hoping that I had missed finding the rare liquid (or solid) phase by looking at a single saw-cut through the experiments, I began quartering every ~4 mm experimental charge in order to get four independent surfaces to analyse. Still no luck.

Also in desperation, I began lowering the temperature of the experiments. I was hoping that some of the totally liquid charges would become partially solid when temperature was lowered. This didn’t work either. All the experiments remained either totally solid or totally liquid.

There is an apocryphal story about a frog that is placed in a pan of water. The water is heated slowly enough that the frog doesn’t really notice the temperature change until it becomes frog soup. The antithesis of that procedure was my continual lowering of the temperature of the Ge experiments. One day



I finally realised that I was ~50 °C below the Fe-Ni solidus; and I still did not have two phases in any experiment. Something was badly wrong. The frog should be frozen at those temperatures.

The most obvious solution to this issue was that there was a nucleation problem. I was 50 °C below the Fe-Ni solidus and charges were either all solid or all liquid. So, a certain logic proceeded from that observation. If a solid nucleated, then the whole charge solidified. If that nucleation event never occurred, the charge remained molten.

My experimental protocol had been to take my charges to about 100 °C above the liquidus for about 24 hours to homogenise the charge and then drop to run temperature and hold there for about 48 hours. Perhaps 24 hours above the liquidus had destroyed all nuclei, making later crystallisation problematic? I would not have expected such in a metallic system; but the next set of four experiments were simply taken to the run temperature (~1495 °C) for a couple of days. All four charges had both solid and liquid; and the partition coefficients from all four charges agreed well. Problem solved. I think Mike Drake then began to accept me as an OK post-doc. And it was a lesson that sometimes you can be *too* careful in your experimental protocol. I would have to relearn that lesson several times afterward.

5.2 Partitioning in the Fe-Ni-S-X(Tracer) ± P System

Part of my early post-doc duties, since Drake was on sabbatical, was to oversee a trio of undergrads who were working with Mike. One of these was a geology student, Paul Jamrog. Paul did not really understand the science of what he was doing in the lab, but he was good with his hands. He routinely repaired his car, an old VW.

Paul was doing Ge-partitioning experiments in the Fe-Ni-S system using sealed silica tubes near the Fe-S eutectic temperature (~1000 °C). He and I were working on totally different ends of the ^{Ge}D temperature spectrum, about 500 °C apart. Eventually, Paul produced an experiment with both solid and liquid, which I then analysed, using the electron microprobe. The ^{Ge}D that I had measured near 1500 °C in the Fe-Ni system was ~0.6. The ^{Ge}D from Paul's experiment was about 300! There was so little Ge in the Fe-S liquid that it was difficult to measure with the electron probe, and further analysis later lowered that value to about 150. But suddenly, the presence of S seemed to be very important. And suddenly, Mike was not about to abandon solid metal/liquid metal partitioning.

The effect of adding S to the experiments was striking. As we collected more data, we found that the $D_{\text{sol met/liq met}}$ for elements like Ir increased faster than exponentially as S was added (Fig. 5.1). This became a challenge to explain and parameterise. We were not the first group to report this type of behaviour. Willis and Goldstein (1982) looked, not only on the effect of S, but also at the



effects of C and P on siderophile element partitioning. But we eventually did publish our Fe-Ni-S results (Jones and Drake, 1983) and later expanded into the Fe-Ni-P and Fe-Ni-S-P systems (Malvin *et al.*, 1986).

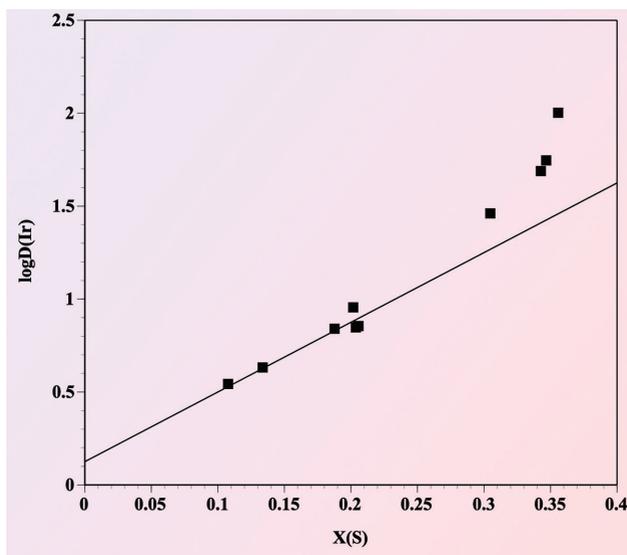


Figure 5.1 $\log D_{\text{sol met/ liq met}}^{\text{Ir}}$ vs. mole fraction sulphur in the metallic liquid. The non-linearity of the trend indicates that D is increasing faster than exponentially. Line is for reference only.

5.3 Meddling with Metallurgists

As the experiments in the Fe-Ni-S-P systems began to show interesting results, Drake went to the UA metallurgy/materials science department to quiz them about melts in this system. Their response was to invite him to give a seminar on the subject. This was not what we had hoped for. We wanted the information transfer in our direction. However, this introduction to the materials science department gave us an entrée into the metallurgical world. I later sat in on a class in physical metallurgy in that department. My first observation was that geochemists and metallurgists used different words for the same equations.

But my real introduction to engineers came just a bit later. After I started to believe that I was beginning to understand Fe-Ni-S partitioning, I took some of my plots over to an engineer for him to look at. He was rather skeptical but said that he would be willing to look into the problem. I should bring him all my data and give him a week to think about it. So I did. And after a week he pronounced



the whole matter hopeless. He could do nothing with the data and wondered why I had not kept this or that variable constant. As I recall, I left the engineering building feeling a bit anxious, but overall, I was confident in my own approach.

One of the reasons I became a user of MacIntosh computers was because, in the mid-80's, I was working on five different machines: (i) one ran the electron microprobe, (ii) one acted as a combined word processor/simple calculator, (iii) there was a Drake group MacIntosh that also acted as a word processor, (iv) my collaborations with Lon Hood used the Chuck Sonnet group computer, and, (v) Bob McMillan (another post-doc at LPL) graciously gave me access to the Spacewatch Computer that helped to detect near-Earth asteroids – on weekends, I think. But Command-C meant something different on each computer. It became confusing, so I ultimately retreated into the MacIntosh world with pull-down menus, where I didn't have to remember Command-keys. Importantly, Bob was willing to let me use his computer so that he could claim (legitimately) that his hardware was not just searching for doomsday asteroids, but that it was also doing interesting geochemistry.

I needed a computer that would plot data, and the Spacewatch Computer could do that. This was the only computer I had access to that would draw plots – at least as I recall. Plotting data, using a computer, was not routine at the time. The method I used was trial-and-error. Plot something against something else and hope for a straight line. If that didn't work, plot something against another something else.

Although that was how it worked in practice, there was a modicum of method to the madness. I had already attempted to understand our $^{67}\text{D}_{\text{sol,met/liq,met}}$ data using a very simple regular solution model for the liquid (Hildebrand, 1929). And although I do not remember the details, at some point I decided that using a regular solution for Fe-Ni-S liquids was not an internally consistent explanation. So I made up a different model that I termed “non-metal avoidance.” The basic idea was that, as a S atom was added to the liquid, it gobbled up a site that was previously available to Fe, Ni, or Ge. In addition, there was a theoretical paper (Sharma and Chang, 1979) that postulated that most of the S in an Fe-S liquid existed as a real FeS species. Therefore, sulphur did not just gobble up a single site, it gobbled up two: its own and the Fe it strongly bonded with. Therefore, the eventual form of the plots I made was $\ln ^{67}\text{D}$ vs. $\ln (1-2X_S)$, where X_S was the mole fraction of sulphur in the liquid. There was a correlation, but it was still non-linear, so more fiddling was required. The final equation became

$$\ln ^{67}\text{D} = \ln ^{67}\text{D}_o + \beta_{\text{Ge}} \ln (1 - 2\alpha X_S) \quad (5.1)$$

where α was a constant determined by trial-and-error, β was the slope of the data array after it had been linearised by an appropriate α and D_o was the solid metal/liquid metal partition coefficient in the S-free system (Fig. 5.2). The magnitude of β was proportional to the strength of the Ge-S repulsion. The α term was interesting in that it could be interpreted as an activity coefficient for FeS. The α value of 1.09 seemed to be a property of the Fe-Ni-S system, not the trace element, and was similar to the value of an activity coefficient (γ) that would be required



to make FeS have unit activity at the Fe-FeS eutectic ($\gamma_{\text{FeS}} = 1.12$). Equation (5.1) also suggested ways to model D's in more complex systems, such as Fe-Ni-S-P. But my UA engineer had never seen this type of equation before, so it didn't pass muster in his eyes. One of my JSC colleagues once pronounced that engineers have "one-bit resolution." There may be some truth to this.

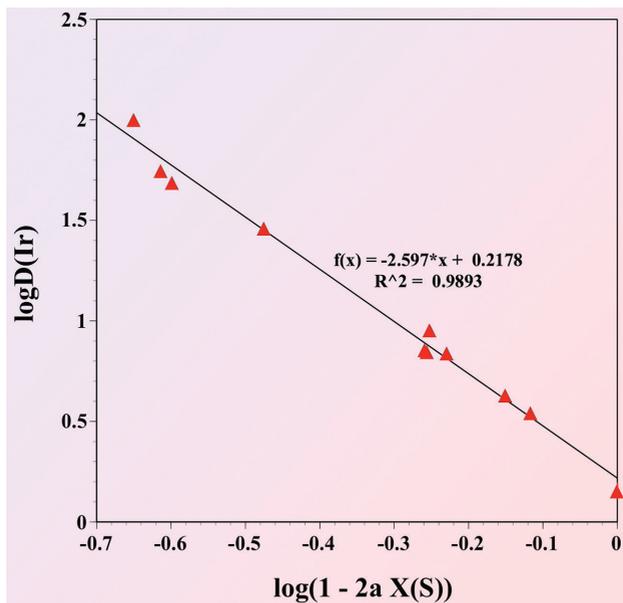


Figure 5.2

$\ln D_{\text{sol met/ liq met}}$ vs. $\ln(1-2aX(S))$. Linearisation of the data in Figure 5.1 is achieved by a model where Ir avoids sulphur species in the metallic liquid (Jones and Malvin, 1990). See text.

The Spacewatch Computer plots eventually led to Jones and Malvin (1990). Dan Malvin was a grad-student in Mike's group who significantly contributed to the paper in two very different ways: (i) he had performed most of the experiments in the Fe-Ni-S±P system (Malvin *et al.*, 1986); and (ii) he used a clever series expansion of $\ln X$ that related equation (5.1) to equations that engineers were more accustomed to. Dan suspected that his association with Mike and me was a true karass (*cf.*, Vonnegut, 1963) because the initials on our 1986 paper formed a palindrome: DJMJHJMJD. Personally, I'm not sure; karasses are a tricky business.

Because the engineers had tried to be helpful to us, Dan and I submitted our results to *Metallurgical Transactions*, an engineering journal. We were trying to help them. This became painful for everyone concerned. The editors and reviewers had never seen an equation like ours before, and it contained no standard intensive variables such as temperature and pressure. So much for



trying to help the engineers. It eventually did get published, but this may be the only paper that I've never received a reprint request for, although I realise this comment dates me.

Siderophile trace element partitioning in the Fe-S system is an extreme example of a system where non-ideal interactions are often so intense that ideal variables such as temperature do not really contribute. Even my *Met. Trans.* editors had to admit that multiple regressions of $\ln \text{ } ^{\text{C}}\text{D}$ data that included temperature as a variable did not improve the fit. Further, remembering the above discussions concerning heats of fusion, ideal temperature effects are weak because ΔH_{fus} for metals are ~ 4 kcal/mole. So, for multiple reasons, temperature was not an important variable, except to the metallurgists.

5.4 Soret Effect in Metallic Systems

By 1984, Mike and I were in a somewhat heated debate with Joe Goldstein (Lehigh University) and his post-doc, Ram Sellamuthu. Trace element partition coefficients between solid and liquid metal were being measured and reported by both the Drake and Goldstein groups. Unfortunately, the results from these two groups did not agree well (e.g., Malvin *et al.*, 1986).

There were big differences in experimental protocols between these two groups. The Tucson group placed charges in a furnace at the desired temperature and held them there until it appeared that equilibrium had been achieved. The Lehigh group performed their experiments by a crystal pulling technique (Czochralski growth). This method extends the length of the crystal incrementally as it is pulled from a hotter region of the furnace into a cooler zone. The Lehigh group believed that equilibrium would be maintained at the solid-liquid interface and that the trace element profile along the length of the crystal would preserve a fractional crystallisation trend. From this profile D's could then be mathematically extracted.

At the 1984 Meteoritical Society meeting in Albuquerque, NM, our two groups met privately and attempted to hammer out our experimental differences. My recollection is that, after that session, Goldstein understood that his post-doc's experiments did not agree with well-established phase diagrams. Drake disagreed with me on this point. Only Goldstein knew for sure.

Czochralski growth was, in principle, a very elegant means of following a liquid line of descent for iron meteorites. However, a possible experimental difficulty with the Lehigh experiments was that the interface between the crystallising solid and the remaining liquid was positioned at an extreme thermal gradient – by definition. Thermal gradients were known to fractionate elements (*i.e.* the Soret effect); and Mike and I were not convinced that the liquid composition at the Lehigh solid-liquid interface was the composition that simple equilibrium would have predicted.



A few years earlier, Dave Walker (Columbia University/Lamont-Doherty Geological Observatory, now Earth Observatory) had pioneered Soret diffusion studies in silicate systems – *i.e.* the effect of a temperature gradient on liquid compositions within an initially chemically homogeneous experimental charge. Because we believed that the Sella-muthu experiments might have been compromised by his steep thermal gradients, Mike essentially invited us (*i.e.* me) to Walker’s lab to perform Soret experiments on a metallic system. Dave graciously accepted our invitation.

I have described above how disheartening my first few months were as a Drake post-doc. However, these early Tucson days pale in comparison to my three weeks in Walker’s lab. No experiment ever came even close to working. With hindsight, I went to Lamont with an experimental recipe that was designed to fail. I did not know this (obviously). So I spent all my time there beating my head against a wall and working against a finite schedule, while living out of a motel room in beautiful South Nyack, NY (note sarcasm). So the trip was a complete failure, except that I learned a little bit about how to perform piston-cylinder experiments. I left Nyack downtrodden.

However, unbeknownst to me, Walker kept plugging away at these experiments, and a few years later I received a letter with a metallic Soret experiment enclosed. All I had to do was to analyse it. With another experiment, this resulted in a short paper on Soret diffusion in metallic systems (Jones and Walker, 1991a).

5.5 Dave Walker

At this juncture it may be helpful to comment on my interactions with Dave Walker. I have had several fruitful collaborations with Dave, most of which will be described here. Although my first visit to Lamont was stressful and extremely unproductive, Dave didn’t write me off. I suspect that was because he despised the thought that experiments in his lab had failed. But because he persevered with the metallic Soret experiments, we afterwards had other chances to collaborate. When I first arrived at JSC, there was really no high-pressure lab, so for several years I spent a few weeks each summer at Lamont-Doherty. I found that, being away from JSC, I could get a lot of experiments done in a relatively short time. Nobody knew where to find me.

One of the things I remember is that Dave was probably the first person to teach me how to design an experiment. Before that, I had basically relied on rote recipes, so this was a very educational experience. Experiments are never perfect, but with some thought, it ought to be possible to design a good experimental attack. My philosophy has become: “If enough thought is given to the first experiment, the second experiment should always work.” Sometimes, that actually happens.



I think that Dave would not mind me saying that he can be a rather opinionated person. And that, having the courage of his convictions, trying to change Dave's mind is *more than somewhat* difficult (*cf.*, Runyon, 1937). I confess that I'm probably not terribly different. Therefore, I regard it as a singular success that I once managed to change Dave's view on a very narrow issue regarding Soret diffusion. Simplifying the story, Walker was adamant that knowing the bulk composition (*i.e.* major elemental composition) was insufficient to predict the Soret behaviour of a trace element. But Chip Lesher (UC Davis), one of Dave's former students, had advocated just the opposite.

One night while visiting Lamont, I couldn't sleep, so I got up and began deriving an equation that addressed this Soret issue (Jones and Walker, 1991a). Dave found the derivation on his breakfast table the next morning and eventually approved of it. I'm sure Chip instinctively knew the correct answer, and I'm also sure that it was Chip who had pointed me in the right direction. But Chip had never given Dave a derivation. Therefore, I got some credit from Dave that probably should have belonged to Chip.



6.1 Partitioning between Metals and Silicate Liquid

My recollection is that, in 1981, Drake attended a workshop on igneous processes at the Stillwater (Montana, USA) layered intrusion. He came back saying that Ed Stolper (Caltech) had suggested that we add a silicate liquid to our Fe-Ni-S solid-metal/liquid-metal experiments. I immediately came up with several good reasons for why this would not be helpful. I think this was at least because I had no idea what experimental capsule to use. We had been using alumina (Al_2O_3) crucibles for both the Fe-Ni and Fe-Ni-S experiments. Adding a silicate liquid to the charge would certainly result in reactions between the silicate liquid and the alumina. What I failed to recognise was that, in the total absence of data, an imperfect experiment was better than no experiment at all. Suffice it to say that Drake won that argument. We continued to use alumina capsules.

So, serendipitously, I suddenly found myself in the right place, at the right time, with a very interesting project. And I had a set of skills that served the project well:

First, I had the ability to do the experiments that were required. Although I had not yet learned how to seal modestly large (~12 mm), evacuated silica tubes, I could certainly put them in the furnace and quench them later. Initially, we used glassblowers in the Chemistry Dept. at UA and, later, a small firm in Phoenix, AZ to seal the tubes. But I slowly learned how to seal tubes myself with guidance from Bill Boynton (UA).

Second, it was necessary to evaluate the experimental charges for equilibrium using the electron microprobe; and this I could also do.

Third, the silicate glass needed to be separated from the metallic phases. This was somewhat tricky. I would break up the charge with a big hammer and tenaciously look at individual silicate shards under a binocular microscope, in order to avoid those glasses that had adhering metal, sulphides, or alumina. Sometimes, I could see sulphide or metal precipitates(?) on what had probably been a free surface of the silicate, and these were rejected. Adding ~100 mg of silicate powder to a charge usually resulted in only a few milligrams of suitably clean silicate glass. The largest $D_{\text{sol met/sil liq}}$ we were able to measure was $\sim 10^6$, which suggested that my selection criteria were reasonably sound.

We soon began to evaluate the purity of our glass by doping every charge with Ir, which had a very large $D_{\text{sol met/sil liq}}$ ($>10^5$). The quality of another trace element D in the same charge could then be evaluated by the size of ${}^{\text{Ir}}D_{\text{sol met/sil liq}}$. Further, Ir was rather easy to measure by neutron activation analysis.



Fourth, for those tracers that were too low in abundance to analyse with the electron probe, we needed to perform neutron activation (INAA), *i.e.* there were no quantitative ion probes or LA-ICPMS instruments. But fortunately, a lot of my past background had been concerned with radio-analytical techniques. And in a very few cases, we managed to get agreement for metal/silicate D 's using both the electron probe and INAA, which was extremely gratifying. Further, Bill Boynton's neutron activation labs were just down the hall from our furnace room.

So I found myself in the right place, at the right time, and with some of the right skills. Sometimes it's better to be lucky than good.

There had been earlier metal/silicate partitioning studies, but none of these had included a non-metal, like sulphur. One was Kimura *et al.* (1974); another was Werner Rammensee's thesis (University of Mainz, Germany). Even today, Rammensee's thesis work is still of interest (Rammensee, 1978).

However, the Kimura experimental results seemed odd. He had performed liquid metal/liquid silicate experiments for Re at the Ni-NiO buffer; but the $^{Re}D_{met/sil}$ seemed much too high for that f_{O_2} . There was too little Re in the silicate, as far as Mike and I were concerned. Consequently, Mike asked Ed Anders (University of Chicago) if he would send us an aliquot of Kimura's silicate glass, and Anders graciously agreed.

Immediately, looking at Kimura's experimental charge, I could see that the experiment had not been performed at Ni-NiO. Under those rather oxidising conditions, the glass should have been black because of Fe^{3+} - Fe^{2+} charge transfer. In actuality, the glass was green, indicating that little, if any Fe^{3+} was present in the glass. I think I made a brownie point with Drake that day, but only because I had taken a spectroscopy course from George Rossman as a grad-student. And, yes, electron probe analyses of the Kimura glass later confirmed my initial prejudice; at high f_{O_2} there should have been percent levels of NiO in the glass, but there wasn't. Kimura had apparently not considered the possibility that, even though his experiments were performed in a Ni capsule, his f_{O_2} could have been much lower than Ni-NiO.

6.1.1 *On being too careful*

Above, I discussed an instance where being too careful with a thermal history resulted in bad experiments. Here is another example of that.

When I began to perform metal-silicate partitioning experiments, I wanted to closely control the f_{O_2} . Therefore, in addition to the experimental capsule, I would also add a capsule with iron metal powder in a silica tube. The intent was to buffer the experiment near the silica-fayalite-iron (QFI) oxygen buffer. At these temperatures, fayalite was not a stable phase, but would exist as a liquid. Therefore, the charge was not exactly at the QFI buffer, but it should have been close.



For reasons I do not remember, I once analysed the iron metal from the buffer capsule. The experiment had been for Ge partitioning. The upper few microns of the buffer metal contained Ge at almost exactly the same concentration as the Ge in the metal of the experimental charge. I had inadvertently performed a reversal experiment by vapour transport from the experimental charge to the buffer charge.

This result was very much a double-edged sword. I was gratified that there was experimental evidence of communication between the sample and the oxygen buffer, but I was concerned that the buffer was complicating the equilibrium between silicate and metal in the experiment. At that point I stopped using a buffer capsule. I had been too careful.

Henceforth, our experiments were self-buffered by their metal-silicate liquid assemblage; and f_{O_2} was calculated later by measuring Fe in the metal, FeO in the silicate glass, and assuming ideality. This calculation could have been wrong by a factor of two, but a factor of two is only 0.3 f_{O_2} log units, which is not terribly different from quoted errors for log f_{O_2} determinations using electrochemical cells (e.g., Jurewicz *et al.*, 1993b). Later, Valerie Hillgren, a student of Drake's, showed that this type of calculation would yield a ΔIW estimate that was independent of pressure (Hillgren, 1993). To me, this result was very surprising, but I was able to reproduce her derivation.

6.2 Jones and Drake (1986)

The result of our metal/silicate partitioning experiments was that Mike and I published a review paper on terrestrial core formation in *Nature* (Jones and Drake, 1986a). I have to admit that I have never been totally happy with that paper. It took a long time to write (about two years), and it was unsatisfying in several ways.

To help clarify that statement, let me give some background. In the 1960's Ted Ringwood noted that the Ni content of the Earth's upper mantle was much too high to be consistent with metal-silicate equilibrium (Ringwood, 1966). Following on that observation, several authors suggested that undifferentiated meteoritic materials had been added to the Earth during and after core formation (e.g., Wänke, 1981). This concept has been described both as the late veneer (to explain the highly siderophile elements, such as Ir) and as heterogeneous accretion (to additionally explain moderately siderophile elements such as Ni and W e.g., Morgan, 1986; Wänke, 1981). The important point is that abundances of moderately siderophile elements (e.g., W, Ni, Co) and highly siderophile elements (e.g., Ir, Os, Pt, Au) were both much, much, too enriched in the upper mantle for there to have ever been even a modest equilibration with metal. Since the Earth does have a metallic core, this observation was a problem. Essentially, that issue still remains, although there is a school of thought that high pressure and temperature may ameliorate this problem (e.g., Li and Agee, 1996).



But back to my discomfort: Mike and I had advanced a model to explain the high abundances of siderophile elements that we termed “inefficient core formation,” which had also been suggested by Arculus and Delano (1981). Our analogy to this model was that of petroleum extraction from a reservoir – it’s hard to get absolutely all the oil out, fracking or not. So it seemed reasonable to us that extracting a core with 100 % efficiency would be difficult.

And this became my first dissatisfaction with the paper. I attempted to model a suite of eleven elements for which we had experimental data (P, Co, Ni, Ga, Mo, Ag, W, Re, Ir, Au, and Pb) using the inefficient core formation model. My best modelling result was that there should be a lot more S in the mantle than mantle xenoliths or basalts would indicate.

The failure of the model was disheartening for two reasons: (i) we had publicised a model that didn’t seem to work quantitatively; and (ii) I really disliked the late veneer model, which was the only alternative at the time.

My problem with the late veneer was that it had to be mixed into the mantle so well that this veneer had to have been homogenised down to the hand specimen scale. Iridium contents of spinel lherzolites from around the world are fairly boring (*e.g.*, Basaltic Volcanism Study Project, 1981). We now know that my view at that time was somewhat oversimplified – systematic variations exist between Ni/Ir and Ir (*e.g.*, Jones and Palme, 2000); but even the Ir variation for spinel lherzolites documented in Jones and Palme (2000) is limited to 4 ± 2 ppb. I believed in 1986 that the probability of mixing an accretionary veneer into the mantle to the hand-specimen scale was nearly impossible. I still believe that, and I have seen no evidence to contradict that belief. Therefore, the quantitative failure of an endogenic model (inefficient core formation) to counter an exogenic model (late veneer) was very disappointing.

Perhaps the failure of the inefficient core formation model was due to my being overly ambitious. I tried to fit a lot of elements, which had very different siderophile, chalcophile, and lithophile tendencies, using a single model. While I believe that this was scientifically honest, it may have been a *bridge too far* (Ryan, 1974). Instead, it might have been worthwhile to attempt modelling subsets of those elements. Perhaps again, I had been too careful.

Another reason I was unhappy is that our “best fit” inefficient core formation model required ~10 % silicate partial melting. Our suite of models varied several parameters, one of which was the proportion of silicate liquid, which varied up to 20 %. I felt rather guilty about this, because it seemed to me that the amount of silicate liquid at the time of core formation had to be very much lower, based on the worldwide occurrences of fertile spinel lherzolites. In terms of major lithophile elements, these samples are nearly chondritic (*e.g.*, Jones, 1996). But I rationalised to myself that we knew so little about core formation that this amount of silicate partial melting was not unreasonable.

The next two sub-sections treat these issues in somewhat more detail.



6.3 The Giant Impact Model for the Moon

But my dissatisfaction with 10 % silicate partial melting pales in comparison with my dissatisfaction with terrestrial magma ocean models.

In the early 1980's it was advertised that there would be an Origin of the Moon conference in Hawaii, so that researchers could have sufficient time to prepare contributions. Mike Drake and Clark Chapman (Planetary Science Institute, PSI) decided that there should be a joint UA-PSI contribution, with PSI supplying the physics and UA supplying the chemistry. In principle, this was a great idea, and every week we would get together and discuss the science.

In practice, though, this was really hard. I had great difficulty communicating with Rick Greenberg, a PSI scientist. It usually took a Clark Chapman translation to communicate with Rick, even after I thought I had reiterated what Rick had just said, but just using different words. Further, after we had decided on a particular model of lunar origin to explore (we termed it “the circumterrestrial disk model”; Weidenschilling *et al.*, 1986), Bill Hartmann, another PSI scientist, always wanted to change the subject to giant impacts. I found neither of these complications helpful.

But the main result of the Origin of the Moon conference was a general acceptance of the Giant Impact model, where a Mars-sized planetesimal collides with the Earth and spawns a Moon from the resulting ejecta. Unfortunately, I have never been able to embrace this model. And the reason stems from the fact that I distrusted my Jones and Drake (1986a) core formation models that required large degrees of silicate partial melting (~10 %). I have not yet changed my mind on this, but Drake eventually accepted the Giant Impact model. I see no evidence in our terrestrial rocks that the Earth has experienced a magma ocean (Jones, 1996). And since some form of a magma ocean must surely be a consequence of a Giant Impact, I seriously question the Giant Impact model. In the end, the rocks must decide, not the models.

I am not unmindful that some isotopic data on real rocks [especially ^{142}Nd (^{146}Sm decays to ^{142}Nd with a half-life of ~100 Ma)] lend credence to a very early terrestrial differentiation event. However, there seem to be two competing philosophies about ^{142}Nd . The first is that the terrestrial ^{142}Nd anomaly is due to an early differentiation. The second is that the Sm/Nd ratios of the Earth and Moon were both inherited from a non-chondritic reservoir, and therefore, the Earth and Moon now have reservoirs with similar ^{142}Nd anomalies. Bottom line: this topic requires much more discussion than I have the ability to address here.

To be more specific, there are several fertile, mantle-derived spinel-xenoliths that seem to mitigate against a terrestrial magma ocean and, therefore, put the Giant Impact model for the origin of the Moon into question. I used one of these, UM-6, from the Basaltic Volcanism Study Project (1981) as an example (Jones, 1996). It has nearly chondritic major element abundances, nearly flat HREE elements, and nearly chondritic HSE relative abundances. The question



is whether these characteristics are a primordial signature or whether they have been produced by subsequent mantle processing (*i.e.* mixing or metasomatism). Personally, I find it much more plausible that these samples are rare remnants of nearly primitive mantle. Otherwise, elements with very different chemical tendencies are required to behave coherently during magma ocean crystallisation or during mantle metasomatism. Most geophysicists, I believe, view the Giant Impact and a subsequent terrestrial magma ocean scenario as an opportunity to homogenise. I view that scenario as an opportunity to differentiate.

In terms of major elements alone, I question whether the physical situation after 80 % crystallisation of a terrestrial magma ocean would be much different from that of 20 % partial melting. By the time a magma ocean has reached this stage of crystallisation, its turbulent, efficient mixing regime should have ended (*e.g.*, Tonks and Melosh, 1990) – the system should have “locked up.” I think most petrologists would argue that 20 % silicate partial melting should be sufficient to separate a basaltic liquid from its source region – *e.g.*, komatiites. So, I believe it is reasonable to ask as to how a solidifying magma ocean can preserve nearly chondritic relative abundances of HSE elements and moderately compatible refractory lithophile elements (*e.g.*, HREE) while basaltic liquids are being removed to the crust, or elsewhere. To date, I have not received a satisfactory answer to this question, except perhaps from Dan McKenzie (Cambridge University), who says it’s not possible.



7.1 Alkali Volatility

Mike Drake had an undergrad for a summer, Melanie Kreutzberger, who produced a nice set of experiments on the volatility of alkali elements. A Di-An-Ab glass, doped with Na, K, Rb, and Cs, was suspended in a furnace for different time durations and the volatile loss of these elements was then measured using the electron microprobe. In our experiments Cs was the most volatile, but this did not seem to be reflected in the Rb/Cs ratios of lunar rocks. Therefore, we argued that our experiments were not consistent with the ideas of Ted Ringwood (ANU) who advocated that the Moon had mainly inherited its geochemical signatures from the Earth (Kreutzberger *et al.*, 1986).

This set up a series of papers, comments, and replies between the Tucson/JSC, Canberra, and Mainz groups (Jones and Drake, 1986b; Ringwood, 1986; McDonough *et al.*, 1992, 1994; Jones and Drake, 1993, 1994). This was probably one of those instances where more heat than light illuminated the basic issue. Still, the establishment of the Moon's abundances of volatile alkali elements should, in principle, be an important constraint on the origin of the Moon (*e.g.*, Humayun and Clayton, 1994; Albarède *et al.*, 2015). For example, the Humayun and Clayton paper emphasised that the K isotopic compositions of almost all bodies in the inner solar system were nearly identical. It is not out of the question that forming a volatile-depleted Moon by a Giant Impact event might result in some degree of differential K isotopic volatilisation, but the observed K isotopic compositions of the Earth and Moon are indistinguishable.

7.2 Partitioning between Pt Metal/Silicate Liquid, and More Nucleation Issues

The nucleation issues in the Fe-Ni-X system discussed above were not my first experience with such problems. During my thesis, Burnett wanted me to do an experiment at very low f_{O_2} , to make sure that all the Pu in the experiment was in the 3+ valence state. In our Co-CoO-buffered experiments, some Pu could still be 4+. Uranium, Th, and Sm were also included in this set of experiments.

The first experiment, in an evacuated, sealed silica tube, with a graphite capsule, grew no diopside, but it had been designed to do so. From my previous experiments, I had noticed that a lot of my diopsides had grown attached to the Pt capsule. Therefore, I decided to add a piece of Pt₉₅Au₅ foil to the charge so as to provide nucleation sites. This worked; diopside usually crystallised thereafter, but I did not particularly notice that the Pt had curled up into a little round ball, or at least I did not notice until the sample was returned from the nuclear reactor.



The round ball of Pt was actually a two-phase assemblage of solid Pt spheres surrounded by a Pt-Si liquid, and the partitioning behaviour of U was clearly indicated by the fission track densities over the solid and liquid. Uranium track densities were high over the Pt spheres and very low over the Pt-Si liquid. Until I had etched the mica detector and looked at the fission tracks, I had no clue as to what the experiment had actually done.

This became my second paper (Jones and Burnett, 1980) and a couple of different tendrils emerged from that study.

7.2.1 *Experimental consequences of Pt (in)stability*

Platinum needs to gain only two electrons in order to have all of its electron shells filled. Therefore, Pt is voracious in its quest for more electrons. It will expend much energy in order to enhance its quantum-mechanical stability. Two experimental consequences of this are that (i) Pt thermocouples are easily poisoned and (ii) alloying Pt with Au (e.g., Pt₉₅Au₅) significantly mitigates platinum's desire to alloy. This is probably the explanation for why silicate liquids may creep out of an unsealed Pt tube, but will remain in place if the tube is Pt₉₅Au₅.

Consequently, S-type thermocouples (Pt-Pt₉₀Rh₁₀) don't endure as well as B-type thermocouples (Pt₇₀Rh₃₀-Pt₉₀Rh₁₀). S-type thermocouples have pure Pt as one of the thermocouple wires, so it is more easily poisoned. B-type thermocouples have both wires as Pt-Rh alloys, making them more resistant to poisoning and probably making them more refractory with respect to high-temperature evaporation, as compared to pure Pt. B-type thermocouples may not be quite as accurate as S-types, but they have more staying power.

I term these observations as making quantum mechanics work at home for you.

7.2.2 *Condensation in the early solar nebula*

One of the things that Burnett and I learned as we were writing the Pt paper was that Pt's desire for electrons could produce some interesting chemical results. For example, the activity coefficient of Zr in Pt was estimated to be $\sim 10^{-12}$ (Brewer and Wengert, 1973). So instead of Zr beginning to alloy with Pt at an f_{O_2} near the Zr-ZrO₂ buffer ($\sim 10^{-30}$), Zr will flirt with the idea of alloying with Pt at f_{O_2} 's of $\sim 10^{-18}$ – a considerable difference in oxygen fugacity. The f_{O_2} of a nebula of solar composition is about 10^{-15} , so Zr condensing as a Pt alloy suddenly seemed possible, and there had been a report of Zr in a Pt nugget in an Allende Ca-Al-rich-Inclusion (CAI) (El Goresy *et al.*, 1978).

Much later, Steve Jurewicz (JSC), Bruce Fegley (Washington University, St. Louis), and I quantified the partitioning of several lithophile elements into Pt (Jurewicz *et al.*, 1995). We used sealed silica tubes and a Cr-Cr₂O₃ oxygen buffer.



Remarkably, this buffer is very similar to the f_{O_2} of a gas of solar composition at igneous temperatures. But in the end, we could not convince ourselves that Zr partitioning into Pt was an important process in the early solar system.

However, Steve's experimental Pt-(lithophile element) alloys proved very resistant to oxidation under more oxidising conditions. The extremely low activity coefficient for Zr in Pt, combined with the resistance of our Pt-Zr alloys to oxidation, strongly suggests that true intermetallic compounds are produced when Pt and Zr alloy. And, once formed, these intermetallics are extremely stable. This observation may have implications for the nebular condensation of other trace elements and the preservation of their host phases.

7.2.3 *An experimental serendipity*

The initial reason that Pt₉₅Au₅ was introduced into our experiments was because I believed we had nucleation problems. However, the reason these experiments were being done in the first place was because Burnett suspected that not all the Pu in our Co-CoO-buffered experiments was in the 3+ valence state. (He was correct.)

The experimental recipe that I used called for putting the doped silica glass in the bottom of a Pt tube, crimping the tube in the middle, and then adding the Co-CoO buffer in a Pt-Au foil container above the crimp. The Pt tube was then welded shut. The reason for choosing the Co-CoO buffer is lost in history, at least to me.

At some point, near the end of my experimental work, I ran out of Pt-Au foil, but I knew where there was more, found it, and continued as before. Only the last few experiments of my thesis work were performed using this new foil, but the buffers looked different after I began using it. They were greenish in colour after the experiment was done. Eventually, I discovered my mistake. The new "Pt-Au" foil actually was a complex alloy containing Cr – there had not been a label on my new source of foil. And as noted above, the Cr-Cr₂O₃ buffer is extremely reducing. If we had indeed been at the Cr-Cr₂O₃ buffer in these experiments, I think they would have failed, because the Si in the experiment would probably have alloyed with the Pt container and the tube would have leaked (the eutectic of the Pt-rich portion of the Pt-Si system is about 900 °C). So I was somewhere between the Cr-Cr₂O₃ buffer and the Co-CoO buffer. Where? I cannot say. But it was certainly much more reducing than Co-CoO, and the ^{Pu}D values changed perceptibly. Using the wrong foil had gotten the desired f_{O_2} result for the reducing conditions of the early solar system.

7.3 [Gordon McKay](#)

Essentially, I was hired at Johnson Space Center by Gordon McKay. Gordon had been a grad-student with Dave Lindstrom, Marilyn (Martin) Lindstrom, Mike Drake, and Bill Leeman at the University of Oregon. Gordon was not my boss



when I came to JSC, but he always contended that it was he who got me my job. My guess is that he was telling the truth.

Gordon and I had already crossed paths. I had applied for a job at JSC that Gordon eventually won. My suspicion is that the fix was in and that I had wasted my time applying for that job. At that time, Gordon was an NRC post-doc at JSC, so he was well known there.

Gordon did trace element partitioning for most of his scientific career, although later he also began to work on phase equilibria and experimental reproduction of textures in natural samples. But, mainly, the work that I wish to discuss here is his pioneering of analytical techniques.

Gordon's forte was not so much experimental as analytical – specifically electron microprobe analysis. He would analyse his experimental run products mercilessly (*e.g.*, McKay, 1986). By the mid-1980's Gordon was "routinely" measuring certain elements (mainly REE) with the electron microprobe that only existed at a few tens of ppm. To do this he had to use long counting times and also perform careful wavelength scans over an x-ray peak and its adjacent backgrounds. In so doing, on a sample of Zagami, Gordon trashed an abstract that I had submitted while I was still in Tucson (Jones *et al.*, 1985), and I had to eat crow at a major international conference, which was painful. But since I had asked him to do the analysis, I couldn't complain.

Another aspect of Gordon's analytical procedure was to fit x-ray spectral peaks to a functional form in order to subtract interferences and background. In an after-hours discussion at JSC, Gordon asked me what functional form was best for fitting x-ray peaks. My response was that the intrinsic functional form was a Lorentzian distribution, but that the act of detecting these x-rays would impose a Gaussian distribution on the Lorentzian. My recollection is that Gordon's eventual best fit to his x-ray peaks was a functionality of 50 % Lorentzian and 50 % Gaussian, so I think I may have helped Gordon that evening.

Another important contribution from McKay was his observation that $^{REE}D_{px/liq}$ depended on the CaO content of the pyroxene (McKay *et al.*, 1986). I later used this idea to parameterise $^{REE}D_{px/liq}$ using $^{Ca}D_{px/liq}$ (Jones, 1995, 2015), but Gordon always hated that parameterisation. My regressions had $\sim\pm 25$ % error bars, and this was not precise enough for Gordon. My view is that a ± 25 % level of precision gives you a good estimate as to what the partition coefficient ought to be, and, if you need to have better accuracy, then you need to do detailed experiments yourself. But Gordon always wanted better precision than that.

Gordon was a very good experimentalist and analyst, and my personal observation is that he was very trusted by the planetary petrology community. If Gordon signed his name to it, you could pretty-much take it to the bank. His relatively young death was both a personal and professional tragedy.



7.4 Partitioning in Very Reducing Systems

For reasons I do not recall, Bill Boynton (UA) and I decided to look at REE partitioning in a very reduced system (Jones and Boynton, 1983). An observation from enstatite chondrites was that REE became chalcophile under reducing conditions (Furst *et al.*, 1982; Floss *et al.*, 1990). The main goal, I believe, was to look at REE partitioning into oldhamite (CaS). I took one of my standard basaltic starting compositions and doped it with a few REE to cover the mass range and, therefore, predict a ^{REE}D pattern. My brute-force means of producing a reducing experiment was to add aluminum foil to a charge that was sealed in an evacuated silica tube. As I recall, CO₂ needed to be flowed on the outside of the tube to prevent atmospheric oxygen from diffusing through the tube and into the sample. This procedure resulted in very messy experiments, but it also broke new ground. As I stated earlier, when little or nothing is known, even an imperfect experiment may be useful.

After a few fits and starts, I managed to produce an experimental charge that had a single ~10 μm crystal of oldhamite (CaS). It also contained two liquids: Fe-S and (Ca,Mg)S. One charge contained four liquids: Fe-S, Fe-Si, (Ca,Mg)S, and a silicate liquid. This was the first experimental indication of how REE might fractionate in a very reducing system, and the fractionations were very large – fractionations as large as $^{REE}D_{\text{gar/sil liq}}$. This work was followed up at JSC by Tammy Dickinson, Gary Lofgren, and Tim McCoy (*e.g.*, Dickinson *et al.*, 1990; Dickinson and McCoy, 1997).

7.5 Markov Chain Models of Partitioning

A project that never got published (or really even got off the ground) was a mathematical model for trace element partitioning with Charles Hostetler, a Drake grad-student. The model was conceptually simple: suppose a silicate liquid and a metallic liquid are in contact, and also that there is fast equilibration within their individual domains, then also suppose a trace element with a $D_{\text{met/sil}}$ of ~1000 is added to this system. To achieve equilibrium, should this tracer be doped as an oxide or a metal? Our mathematical attempt to answer this question was to perform a Markov Chain model, where in each time step, the tracer had either a 0.001 chance of leaving the metal or a 99.999 chance of entering the metal from the silicate. The number of tracers in each phase were registered after each time step and every time these tracers “knocked on the door” of the adjacent phase, they were either accepted or rejected according to a probability, *i.e.* the D .

We never completed this project. However, my sense has always been that the dopant should be in the chemical form in which it is most compatible. If the $D_{\text{met/sil}}$ is 1000, the dopant should be added as a metal – and *vice versa*. Unfortunately, experimental confirmation of this hunch may be very difficult.



8.1 Rama Murthy

In 1991 Murthy (University of Minnesota) published a paper in *Science* (Murthy, 1991) that drove a lot of the core-formation community crazy. Murthy took results from individual metal-silicate partitioning experiments and extrapolated the results to very high temperatures. He believed the results of these calculations explained the high siderophile element contents of the Earth's upper mantle.

In addition to Drake and myself, it also drove Hugh O'Neill (ANU) and Chris Capobianco (UA) crazy. O'Neill and I submitted rebuttals to the Murthy *Science* paper and discovered that *Science* did not view critiques of their published papers favourably. *Science* reserved for itself the right to decide whether such critiques were publishable. However, in the end, our criticisms did get published (Jones *et al.*, 1992; O'Neill, 1992). A follow-on paper (Capobianco *et al.*, 1993) gave our version of the thermodynamics of siderophile element partitioning.

At a meeting, Murthy criticised the Capobianco paper because we had extrapolated experimental data to high temperatures using only two experiments per element (*i.e.* two experiments at different temperatures, which would yield a ΔH , *à la* equation (1.1)). I rejoined that two were better than one and suddenly Murthy became very quiet. However, Drake noted to me afterward that there were probably only three people in the room who knew that it was Murthy who had extrapolated on the basis of one experiment. I had not gotten my message across.

One person who was not driven crazy by Rama Murthy was Dave Walker. Dave saw opportunity in Murthy's calculation. More on this below.

8.2 Fe-Ni-S at Low Temperature

Collaborating with Tim Benjamin (Los Alamos) and Stan Hart (Woods Hole Oceanographic Institution, WHOI), I conducted a series of experiments near the Fe-FeS eutectic temperature. Our main elements of interest were those that had chronological importance in metallic systems: Pd, Ag, Pb, and Tl, *i.e.* the ^{107}Pd - ^{107}Ag , U/Th-Pb, and ^{205}Pb - ^{205}Tl chronometers. The collaborations with Benjamin and Hart were important for analytical reasons. The concentrations of our trace elements in the solid phases of my experiments were very low. Consequently, we attempted to analyse them by using proton-induced-x-ray-emission (PIXE) at Los Alamos and by using the ion probe at WHOI. Still, some of these analyses only gave upper limits to partition coefficients.



One of our major conclusions was that age-dating, using the ^{107}Pd - ^{107}Ag system, was susceptible to isotopic equilibration issues (Jones *et al.*, 1993). One of the tenets of the interpretation of ^{107}Pd - ^{107}Ag ages was that an analysis of “metal” was actually an analysis of metal (Kaiser and Wasserburg, 1983). But, in reality, iron meteorites can contain small sulphide inclusions. Silver much prefers to be in a sulphide phase, rather than a metal phase. So if a radiogenic Ag atom, originating in the metal phase from the decay of Pd, finds a sulphide inclusion as it attempts to diffuse out of the metal, it will likely lodge and remain there. Because of this, very sophisticated mathematical models, such as those of Kaiser and Wasserburg (1983), should be viewed as upper limits to the true Pd-Ag age of the iron meteorite. If radiogenic Ag lodges in a sulphide inclusion, then diffusion rates of Ag in Fe-metal no longer apply.

The bottom line from this study was that petrographic examination of analysed samples is of the utmost importance. But, because iron meteorites cannot be viewed in transmitted light, this crucial examination is usually either difficult or impossible. An analytical alternative would be to measure S on those aliquots of a sample that are used for isotopic dating (J. Chen, pers. comm.). Another possibility is that detailed x-ray tomography might be able to detect small sulphide inclusions in iron meteorite samples.

Jones *et al.* (1993) also measured partition coefficients for other elements (Ni, Mo, Au), but the main importance of the paper was our data for Pd and Ag. Still, we found that our experimental data for elements that were compatible in metal agreed moderately well (at least on a log-log scale) with metal-troilite and metal-schreibersite pairs from iron meteorites. This gave us some confidence that we were not violating Henry’s law by using percent level doping. But, conversely, our experimental data for incompatible elements did not agree well with natural samples. Our interpretation was that incompatible elements were much more susceptible to sampling issues than compatible elements – specifically because sulphide inclusions in the natural samples could severely compromise a calculated partition coefficient.

8.3 Dave Lindstrom

Below there will be more discussions involving Dave Lindstrom (JSC), just as there has already been much discussion of the Leeman and Lindstrom (1978) paper. Therefore, some background on Dave seems deserved.

When I first arrived at JSC, I discovered something of a ready-made family there. I had just come from Drake’s group to be a NASA Civil Servant (Mike Drake commented at my leaving that this would require a redefinition of both “civil” and “servant”). And Gordon McKay, Marilyn Lindstrom, and Dave Lindstrom, who were all at JSC, had all been fellow grad-students with Mike at the University of Oregon. Therefore, I was somehow accepted as an “honorary Oregonian.”



Dave is an excellent analytical chemist who specialised in INAA, even though his thesis work was mainly experimental. At JSC he inherited the “pit,” a lab about 10 metres below the water table in Houston. This was designed to be a low-background, radio-analytical facility. The background from cosmic-ray contributions was several times lower than at sea level. In addition, the pit was walled with dunite (an olivine-rich rock) that was very depleted in radioactive elements such as K and U. Finally, the INAA detectors in the pit were shielded with pre-WWII Pb bricks – *i.e.* having no man-made ^{210}Pb . With these advantages, Dave lowered his sea-level INAA background by about a factor of 10^3 . Therefore, he could measure much smaller samples – analysing masses of tens of micrograms, which he termed micro-INAA. And he used this to his advantage.

Despite being good friends and also having a lot of similar scientific interests, Dave and I can disagree on a lot of things. For example, I don't think he accepts my interpretation of the Leeman and Lindstrom (1978) paper. What can I say? He's wrong about that. 😊 He also seems to have doubts about the importance of crystal-field-stabilisation-energy on trace element partitioning. Regardless, we have had some interesting collaborations that will be described below.

8.4 Sc Partitioning

To summarise the following discussion: Cassi Paslick (Rock Valley College), then an LPI Summer Intern, began Sc partitioning experiments that had relevance to the origin of a suite of asteroidal basalts (*i.e.* eucrites; Jones, 1984b; Jones *et al.*, 1990; Paslick *et al.*, 1990; Hoff *et al.*, 2014). These were then followed up by Vern Lauer (JSC), who tested the limits of Sc solubility in olivine. At about the same time, in conjunction with Dave Lindstrom, a combination of Henry's law studies and statistical thermodynamics suggested melt speciation models for Sc. And, in the present era, Marc Fries (JSC) is pursuing Raman studies of the Lauer Sc-doped olivines to evaluate the effect of Sc on the olivine structure. In short, Sc partitioning seems to have several useful applications.

The Paslick experiments used ~1 wt. % Sc_2O_3 -doped experiments to measure $^{89}\text{D}_{\text{ol/liq}}$ and $^{89}\text{D}_{\text{pig/liq}}$. The results, as applicable to eucrites, basically corroborated those of Jones (1984b), who used literature partition coefficients for Sc. The implications of these experiments were that most main group eucrites were produced by ~20 % partial melting and that there was very little pyroxene left in the residuum. This casts doubt on the ability of a single source region to produce both eucrites and diogenites (diogenites are pyroxenites that appear to be associated with eucrites). More on this below.

Vern's main interest was to look at the effect of adding more Sc_2O_3 to the system (Jones *et al.*, 1995a; Lauer *et al.*, 1996) and there were a couple of interesting outcomes from these experiments.



First, Vern managed to insert ~3 wt. % Sc₂O₃ into olivine. The stoichiometry of these experimental olivines suggests that this Sc is entering olivine by a defect substitution:



where v represents a vacancy. If defects had weight, this would represent ~1 wt. % of vacancies. ☺ Apparently, the olivine structure is very forgiving with respect to vacancies. This observation helps to explain the relative compatibility of other 3+ ions in olivine, such as Cr³⁺ and V³⁺.

But this concentration of vacancies is so large that it is reasonable to question whether the olivine structure is still maintained at high Sc₂O₃ concentrations. For example, laihunite (Fe³⁺ olivine) has its own structure that differs from that of forsterite or fayalite. However, preliminary Raman analyses by Fries on Vern's experiments indicate that these high-Sc₂O₃ olivines still have the orthorhombic olivine structure – they do not have the laihunite structure.

Second, Vern grew an unknown phase at very high Sc concentrations. It almost had pyroxene stoichiometry, but not quite. Single crystal x-ray diffraction by Joe Smyth (University of Colorado) indicated that this new phase was a pyroxenoid that we nicknamed “pyroxscandite.” Its unit cell was about 50 Å in the c direction and consisted of chains of silica tetrahedra that were separated by an M site after every 9 T sites. We thought this was interesting and began to prepare a paper.

Unfortunately, we were not the first to make this sort of compound. Allan Treiman (LPI) thought that this type of pyroxenoid structure reminded him of something he had read before. Our unknown phase had been grown previously by Jun Ito (University of Chicago) in a simpler, Fe-Al-free, Sc-Mg-Si system. Ito termed it Enstatite IV*-9. The IV designation informed that it was not really enstatite, the asterisk denoted that there was no lithium in the system (!), and 9 referred to the number of silica tetrahedra between truncating M sites. We had been scooped by about 20 years. Ito had also grown Enstatite IV*-8 and Enstatite IV*-10 (Takeuchi *et al.*, 1984). Still, it's nice to know that we weren't wrong, and we have Treiman to thank for that.

A third aspect of these experiments is that the stoichiometry described in equation (8.1) requires two Sc ions and a vacancy, if local charge balance is to be maintained. Therefore, to the extent that olivine is an insulator, these three sites must be in close proximity (*e.g.*, Jones and Mackwell, 2006).

Again, percent-level doping brings Henry's law into question. In this regard, Dave Lindstrom did a very interesting analysis. For his thesis work, Dave measured ^{Sc}D_{ol/liq} using percent level doping, but he also performed experiments using natural samples as starting materials that were not doped with Sc. There would be Sc in these basalts at natural concentration levels, so, using his new micro-INAA technique and micro-drilling, he measured ^{Sc}D_{ol/liq} in the un-doped samples. The D's in the doped and the un-doped experiments were the same (Jones *et al.*, 1995a).



This presents an interesting statistical dilemma. If Sc in the silicate liquid is only present at the 10-100 ppm level, what is the probability that two Sc ions will enter a growing olivine within electrical proximity? I believe the probability is low, 10^{-4} to 10^{-5} . However, in a natural sample there may be other 3+ cations such as Cr^{3+} and Fe^{3+} that may serve as a proxy for a second Sc.

But in our laboratory experiments on eucrite compositions at IW, there was very little Fe^{3+} and no Cr. Therefore, even with wt. % doping, the probability of two Sc ions in electrical proximity must be $\sim 10^{-2}$.

This raises the possibility that Sc in a silicate liquid exists as a dimer of two Sc ions. This has been reported for Cr^{3+} (e.g., Colson *et al.*, 1998), so it is not out of the question that the same could be true for Sc. Unfortunately, it's possible that the only means of addressing this issue is by *ab initio* calculations – although, it may be that NMR (nuclear magnetic resonance) analysis could analytically evaluate the presence of Sc dimers in a silicate glass.

8.5 Carbonate-Silicate Partitioning

John Longhi (Lamont-Doherty) proposed that carbonate-rich liquids might be important for partitioning in martian igneous systems (Longhi, 1991). There seemed to be a complementarity for incompatible trace elements between the shergottites and nakhlites (two varieties of martian meteorites). In addition, it seemed to me that, following the lead of Watson (1976), carbonate liquid-silicate liquid partitioning might provide insights into the limits of igneous, incompatible-trace-element fractionations. Carbonatite liquids and basaltic liquids seemed to me to perhaps be more compositionally extreme than even basalts and rhyolites. Further, I had been taught that Arthur Holmes, no less, had thought that carbonatitic volcanism had initiated the igneous activity of the East African Rift. So maybe experiments on carbonatite systems could be important.

And even though Dave Walker had previously bragged about ignoring trace elements, I managed to talk him into performing a series of carbonate-silicate, immiscible-liquid, partitioning experiments. We picked a series of elements (aka Bathpunch) that seemed to have important geochemical implications: Nb, Mo, Ba, Ce, Pb, Th, and U. And because we used a natural ore for our U spike, we also allowed ourselves the possibility of measuring U-decay-series isotopes that were in secular-equilibrium abundances within the ore. So, in collaboration with Mike Murrell and Dave Pickett at Los Alamos, we also received partitioning information on Ra and Pa. For me, at least, this was a rewarding set of experiments (Jones *et al.*, 1995b). To the best of my knowledge, this is currently the only experimental partition coefficient for Pa in the igneous geological literature. 😊



In addition, Dave, using his Soret technique in a multi-component carbonate system, showed that there was very little of a Soret effect in carbonate liquids. In other words, carbonate liquids are rather ideal. This was a confirmation of a regular-solution thermodynamic analysis of carbonate liquids by Allan Treiman, which also showed that carbonate liquids were rather ideal (Treiman, 1995).

A reviewer has queried as to how a lack of a Soret effect indicates ideality. The reviewer's question assumed that the only criterion for producing a Soret compositional gradient was to have a thermal gradient. But although a temperature gradient is necessary for the Soret effect to occur, it is not sufficient. If an element responds to a Soret thermal gradient, it is going to a compositional region where it is "happier." Therefore, in an ideal system, there is no such place where an element is happier. So, non-ideality is also a Soret requirement.

Dave and I also managed to show that the miscibility gap between silicate and carbonate liquids decreased with increasing temperature, as one might expect (Fig. 8.1a). And partition coefficients followed suit – with all D 's approaching unity as the immiscible liquids became compositionally more similar (Fig. 8.1a). We also showed that the partition coefficients were very regular when plotted *vs.* z/r (*i.e.* the ionic strength), where z is the charge on the partitioning cation and r is its ionic radius (Fig. 8.1b). However, this regularity broke down at very high values of z/r . My rationale, which Dave disliked, was that those elements which fell off the D *vs.* z/r trend were cations that were known to form oxygen complexes: Si, Mo, Nb. And because of the near-ideal nature of the carbonate system, the z/r systematics seemed to be largely attributable to the silicate liquid, not the carbonate liquid.

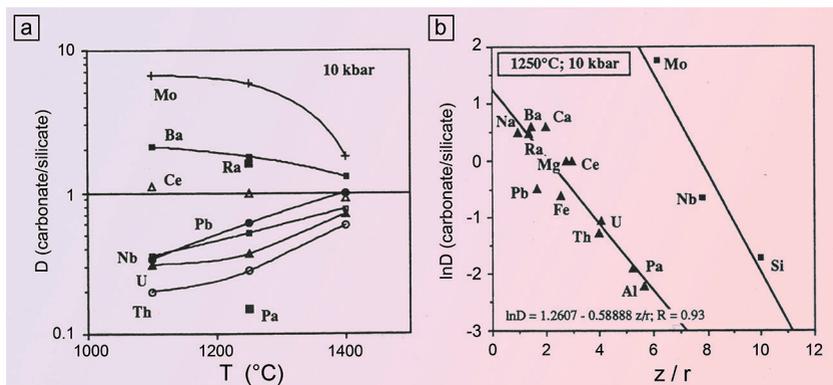


Figure 8.1

Results of carbonate liquid-silicate liquid partitioning. **(a)** $D_{\text{carb liq/ sil liq}}$ *vs.* temperature. As temperature increases, the solvus between the two liquids diminishes and D 's approach unity. **(b)** $\ln D_{\text{carb liq/ sil liq}}$ *vs.* ionic strength (z/r). For ions with low z/r , there is a very good correlation between $\ln D$ and ionic strength. At high z/r , there may be a separate trend. See text.



These experiments were not all sweetness and light. Although our very first experiment worked, there were issues afterwards. After I returned to JSC, Dave performed many more experiments, none of which were successful. Almost all of Dave's experiments leaked out of the graphite capsule and failed in one way or another. I do not remember all the details of what we did next, but I think Dave may have prepared a new starting composition or (more probably) tried drying the composition by grinding it under ethanol and re-drying it. This did not appear to work, so I suggested the same procedure, but using acetone rather than ethanol as the grinding liquid medium. "Pure" ethanol typically has ~5 % water, so acetone seemed more reasonable to me as a drying agent. This appeared to not work either, because Dave's next experiment intruded the thermocouple into the experiment. My best guess was that this last experiment was an aberration and that it should be repeated. Thankfully, this turned out to be the correct approach. The experiments began working again!

But then the Los Alamos analyses suddenly became problematic, just before a scheduled AGU talk. Where there was analytical overlap (*e.g.*, U and Th), the Los Alamos D's did not agree with our microprobe D's. This made me extremely nervous and my concern was passed on to the Los Alamos group, and I may have conveyed my anxiety a little more strongly than I should have. But I had to give a talk that was only two days away. Fortunately, the Los Alamos group had noticed a strange thing when they were extracting the carbonate from the basalt by acid dissolution. The silicate portion seemed smaller than it should have been after the carbonate was leached away. They concluded that their relatively weak acid was not only dissolving carbonate, but also some of the silicate. They then used some mass balance constraints to determine the silicate contribution to the "carbonate" component and suddenly everything agreed. Apparently, silicate glasses with a significant carbonate component are more easily dissolved in acid than are normal basaltic glasses. I had at least 24 hours to finish up my talk and all was good.

A final outcome of this project was that Dave decided to do some high-pressure multi-anvil experiments on our starting composition. The resulting experiment contained augite and Paul Beattie (Cambridge University) performed ion probe analyses on the augite to obtain $^{U,Th}D_{cpx/liq}$. This became another bonus.

8.6 A Review Paper

In the early '90's Tom Ahrens (Caltech) asked me to write a review paper on experimental trace element partitioning for an update of the "red book", a compilation of basic geophysical and geochemical data edited by Clark (1966). This was a lot of work, but fortunately for me, I turned in my draft manuscript in about 1993 before the tidal wave of new partitioning papers emerged in the mid-90's. Trevor Green (Macquarie University), a review author for another journal, was not so lucky, but he did have a better data set from which to write (Green, 1994).



Green's paper appeared before mine, though we never had an opportunity to compare notes during our writing. I think this was for the better. I think of these two reviews as being rather complementary. I would urge a student to read both.

My main new contribution was to parameterise ${}^{\text{REE}}D_{\text{pyx/liq}}$ in terms of ${}^{\text{Ca}}D_{\text{pyx/liq}}$ (e.g., Fig. 8.2). My goal was to provide people with a simple, but useful, set of equations by which they could model REE partitioning (Table 8.1). If you knew enough about your system to know what type of pyroxene was crystallising, you could use ${}^{\text{Ca}}D_{\text{pyx/liq}}$ to model the REE. I also suggested a similar parameterisation for REE into garnet, but there were far fewer data for garnet, and that suggestion does not seem to have held up over time (e.g., Draper *et al.*, 2003). Gordon McKay never approved of that pyroxene parameterisation; and one of my friends once proclaimed these parameterisations to be "*the work of the Devil.*" But my recollection is that, overall, Paul Beattie liked the paper, so I had at least one vote on my side.

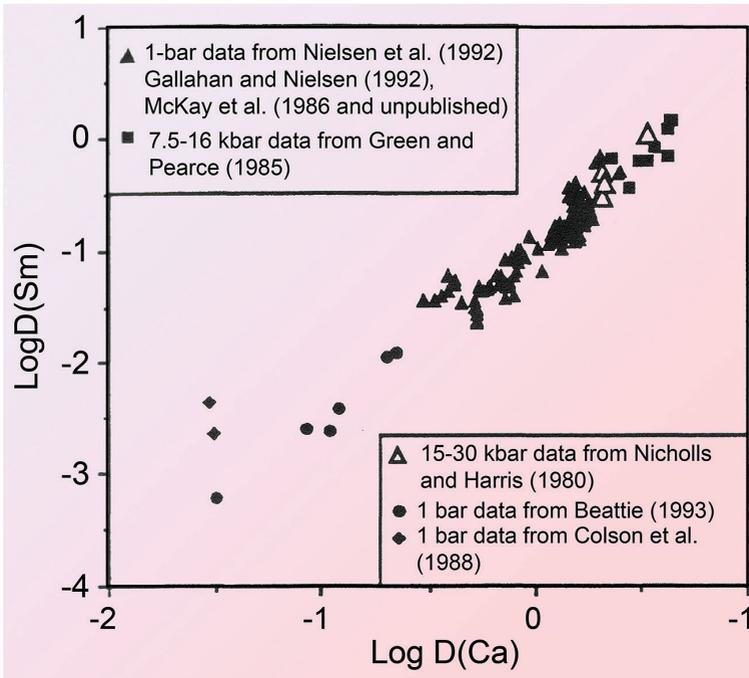


Figure 8.2 In ${}^{\text{Sm}}D_{\text{pyx/liq}}$ vs. In ${}^{\text{Ca}}D_{\text{pyx/liq}}$. Very good correlation between ${}^{\text{Sm}}D$ and ${}^{\text{Ca}}D$ for pyroxenes ranging in composition from orthopyroxene to augite. Outliers at low ${}^{\text{Ca}}D$ are likely due to analytical problems (*i.e.* electron microprobe detection limit).



Table 8.1 Pyroxene/liquid REE partition coefficients near QFM $\log D_{\text{REE}} = A \log D_{\text{Ca}} + B$.

REE	A	B	r^2	$\sigma \log D_{\text{REE}}$	Experiments
La	1608	-1.704	0.799	0.254	96
Ce	1474	-1.695	0.927	0.203	31
Nd	1284	-1.226	0.890	0.072	131
Sm	1388	-0.974	0.900	0.151	205
Eu	0.810	-0.936	0.311	0.052	8
Gd	1.122	-0.732	0.864	0.168	62
Ho	1.106	-0.570	0.894	0.194	49
Yb	0.784	-0.649	0.860	0.116	164
Lu	0.946	-0.740	0.806	0.075	17

8.7 Xenon Partitioning

Although it may not seem so from this memoir, Dave Walker is not particularly a fan of trace elements. But Dave does have a nose for the *path less traveled* (Frost, 1920), and therefore, I managed to talk him into performing Xe partitioning experiments. If ever there was a trace element, Xe must surely qualify.

Our plan was to dope piston-cylinder experiments with crystalline XeF_2 . Other forms of xenon fluoride were somewhat explosive, so the purity of the compound was important. This form of Xe is rather volatile, so adding it to the experiment was tricky. Time was of the essence and Dave was better than I at quickly crimping and sealing the XeF_2 crystal (~2 mm) into the capsule. The odour from the crystal was foul, so adding Xe to the charge needed to be performed in a fume hood. Still, I'm sure I've probably breathed some F_2 or HF as a result of these experiments.

Since we did not have an electron microprobe standard for Xe (duh!), our analysis technique was somewhat unconventional (but tried and true). I would perform and print out a microprobe wavelength scan across the Xe peak. Then I could cut out the peak area and weigh it. Weights from crystals and liquid would then yield an approximate ^{136}Xe . Still, we could say with a straight face that we were on the cutting edge of Xe analysis. ☺

In practice, this type of analysis was rarely necessary because the only solid phase that ever had detectable Xe was graphite (Jones and Walker, 1996). The other solid phases in these experiments were olivine, low-Ca pyroxene, and a silica phase. This was an odd assemblage, to say the least. In the simple, OL-SI-PL pseudo-ternary, this assemblage is not allowed. It is not out of the



question that the silica phase was an immiscible SiO₂ or SiO₂-F liquid, because the phase always appeared spherical, but still, the silica activity must have been rather high. Regardless, it contained very low concentrations of all elements other than Si and it had no Xe either. I once bragged a little too much to John Longhi that I didn't think I was capable of generating olivine, pyroxene, and silica in the same charge. Characteristically, Longhi replied that he thought I was perfectly capable of that. ☺ John has a very vibrant wit.

But our observation that Xe would enter graphite at 1300 °C and 10 kbar, with a $^{Xe}D_{gr/sil\ liq}$ of near unity, suggests that a significant amount of the Earth's "missing" Xe might reside in graphitic shales. At low temperatures, the compatibility of Xe in graphite would presumably be much higher. It's doubtful, though, that this explanation would account for the Xe depletion observed on Mars, which is similar to that of the Earth. Are there black shales on Mars?

8.8 Paul Beattie

Paul Beattie (Cambridge) was a brief, but important flicker in the trace element partitioning community. The several contributions that comprise his thesis and the papers published shortly thereafter are very important. But, for good or for ill, Paul opted for the business world not too long after graduation. He now helps organise Goldschmidt conferences via his corporation.

8.8.1 Henry's law

Paul was one of the first people to seriously use the ion microprobe for trace element partitioning studies. Earlier I described the Harrison and Wood (1980) results, where $^{REE}D_{gar/liq}$ increased at low concentration levels, when analysed using the beta track method. Paul obtained Wendy Harrison's experimental charges and re-analysed them with the ion probe. $^{REE}D_{gar/liq}$ remained constant over the whole concentration range (Beattie, 1993a). The apparent increases in D at low concentrations were almost certainly an artifact of the beta track analytical method, which had complexities that were not understood at the time of Harrison's experiments. My recollection is that Bernie Wood (who, I think, supplied the experimental charges) was rather chagrined over this. This goes back to Don Burnett's feeling that the beta-track technique had been used, but had not been documented analytically.

8.8.2 Partitioning of elements with low D

Beattie also used the ion probe to measure D for elements whose partition coefficients were very low – for example, U and Th partitioning into garnet and clinopyroxene (Beattie, 1993b; Jones *et al.*, 1995b). These experiments have been used to constrain petrologic models of U-Th disequilibrium (e.g., Elliott, 1997),



which provide age information for young, basaltic volcanics. Although there are more recent studies than those cited above, more data on U and Th partitioning would be welcome, in my view.

8.8.3 Olivine partitioning

Beattie followed up on my 1984 olivine partitioning paper in several ways (Beattie *et al.*, 1991; Beattie, 1994): (i) expansion of the literature data set; (ii) an accounting for the presence of ferric iron; (iii) an expansion of the elements modelled; and (iv) a better theoretical underpinning. Paul also showed that the same model also worked for low-Ca pyroxene. Therefore, in general, his was a great improvement on my paper, and I used his results, rather than my own, in my 1995 review paper. However, I would caution readers that, so far, modelling of $^{Ca}D_{ol/liq}$ is problematic. Iron-free systems appear to yield different results than FeO-bearing systems for $^{Ca}D_{ol/liq}$, and silica-undersaturated systems are even weirder.

8.9 Blundy and Wood

One of the most influential papers of the 1990's was that of Blundy and Wood (1994). However, it has been advertised by some as a panacea, which I believe is misleading. What this equation does do, though, is to allow a set of D's for elements, with known ionic ratios (r), to predict D's for other elements that have not been measured – as long as temperature, pressure, and composition are held constant. The D_o of equation (2.3) is not a constant, but is actually a rather complicated variable – $D_o(T,P,X)$. For example, the Draper and van Westrenen (2007) and Gaetani (2004) papers both illustrate how the D_o of the Brice-Blundy-Wood equation depends on the composition of the silicate liquid and/or the bulk composition of the system.

I confess that I have not thought much about this in any detail, but it may also be that the Brice-Blundy-Wood equation can predict how D will change with pressure, provided that temperature and liquid composition remain constant. In principle, it seems to me that the Young's Modulus term might allow this possibility, if its dependence on pressure is known. In practice, though, it is difficult to maintain constant temperature and liquid composition as pressure is changed.

8.10 Ben Hanson, Cr Partitioning, and Reusing Pt Loops

I do not recall what project Ben Hanson proposed to me for his post-doc at JSC. However, once on site, he rapidly suggested that we work on Cr partitioning in Cr-spinel-saturated systems. I agreed because I looked at an old paper by Schreiber and Haskin (1976) at Ben's urging and decided that it couldn't be



correct. There were experiments reported in two different compositional systems that did not show the same f_{O_2} dependence. This smelled fishy to me, and I thought new experiments were needed.

But the bottom line is that, although Schreiber and Haskin may have lost a battle or two, they definitely won the war. Our results, using much newer instruments and techniques, agreed almost exactly with theirs. Only one or two of their experiments seemed wrong to us, and there were perfectly sensible instrumental/analytical reasons for this discrepancy. Our instruments were improved by two decades of time.

These experiments were tedious but Ben showed an enormous amount of patience. Because of the voraciousness of Pt loops for alloying elements, he had to perform three or four saturation experiments on the same loop before he trusted it enough to not take up more Fe or Cr during the final experiment (Hanson and Jones, 1998). Most of these experiments were performed in either the Fo-Di-An or the Fo-An-Si system, so the spinels were picro-chromite, $MgCr_2O_4$. We were essentially duplicating the experiments of Schreiber and Haskin (1976).

Somewhere around the QFM (Quartz-Fayalite-Magnetite) oxygen buffer, the Cr content of the liquid was minimised and thus determined the equilibrium content of Cr^{3+} in the silicate liquid that was saturated with $MgCr_2O_4$. At higher f_{O_2} 's the Cr content rose because of the presence of Cr^{6+} , and at lower f_{O_2} 's it rose because of the presence of Cr^{2+} . Therefore, it was easy then to calculate a Cr^{3+}/Cr^{2+} ratio for geologically reasonable f_{O_2} 's, because the Cr content near QFM was the Cr^{3+} "waterline." And then the $Cr^{3+}D_{ol/liq}$ could be calculated for both Cr^{3+} and Cr^{2+} . The Cr^{6+} experiments were difficult because Cr^{6+} is volatile, as well as carcinogenic, but Ben worked all this out. The results confirmed the Schreiber and Haskin results, gave new clarity to partitioning between different Cr species, and provided standards for subsequent XANES work (e.g., Sutton *et al.*, 1998). And for $Cr^{2+}D_{ol/liq}$, we were able to show that it could be parameterised *vs.* $MgD_{ol/liq}$, the same as for Fe, Mn, and Ni, *à la* Jones (1984a).

For reasons that are still unclear, $Cr^{3+}D_{ol/liq}$ was best parameterised using NBO/T (the ratio of non-bridging oxygens to tetrahedral cations; Mysen, 1983). But in both cases we were able to parameterise our results and those in the literature without recourse to temperature or pressure as variables. In my opinion, this was a very important contribution. Temperature and pressure conditions are almost never known well in natural systems, so compositional parameterisations are, to me, usually preferable.

8.11 Alex Borisov and Rhenium Loops

One of my senior post-docs, Alex Borisov, tackled the problem of Fe-loss to the container rather differently than Hanson, by investigating Fe loss to Re loops (Borisov and Jones, 1999). I suggested this project to him, because I had noticed that some researchers were using Re as a container/heater in high-pressure



multi-anvil experiments, and they did not experience significant Fe loss. It seemed natural to try Re as a substitute for Pt in one-bar loop experiments, where Fe loss was a serious issue (Grove, 1982). Quantum-mechanically, Re was quite different from Pt in terms of its need for electrons; all of Re's electron orbitals are either filled or half-filled. Rhenium has good quantum-mechanical stability.

I don't think Alex really liked this project, though he worked very hard on it and did a much better job than I would have. The utility of Re loops was confirmed, at least at low f_{O_2} , but Re loops are not a total panacea. At high f_{O_2} 's, Re will oxidise to form volatile rhenium oxides and the Re loop will simply evaporate away – and these Re oxides are very toxic. However, depending on the temperature and the experimental duration, Re loops are very useful between QFM and IW-1. We now use Re loops routinely in our lab, unless the f_{O_2} is too high. It saves both time and money. I don't think Alex has gotten enough credit for this study.



9.1 Nancy Chabot and Metals

I probably first met Nancy Chabot (Johns Hopkins Applied Physics Laboratory, APL) in 1997 at the Goldschmidt Conference in Tucson, AZ. Mike Drake was trying to persuade her to come out and have a beer with him and three of his former post-docs. I think he referred to us collectively as “famous scientists.” Regardless, his persuasion failed – Nancy had better things to do. The next year at the 1998 Dublin Meteoritical Society meeting, Nancy tried to convince me that some textures in her experimental charges were due to immiscible Fe-Ni-S-P liquids. That persuasion didn’t work either.

But I later did get to know Nancy better when she came to JSC as a post-doc with Carl Agee (University of New Mexico, UNM). In his management position as our JSC Division Chief, Carl was pretty busy, so Nancy often came by to consult about whatever was happening that experimental day.

9.1.1 Immiscible liquids

The issue at the time of the Dublin meeting was that, based on the Fe-S-P phase diagram, there *should* have been immiscibility in some of Nancy’s experiments, but there wasn’t. This is a problem that is still not completely resolved, although we do have a working hypothesis about how to mitigate liquid immiscibility in this system.

A first guess might be that we should perhaps not expect the simple Fe-S-P phase diagram to pertain since, in Nancy’s case, the system was actually Fe-Ni-S-P-Ag, if I recall correctly (Chabot and Drake, 1997). But Ni behaves so much like Fe in this system that it was difficult to envision Ni as being the culprit. And trace elements were present only at the ~1wt. % level. A better answer seemed to be that there was always some oxygen present in the metallic liquid and FeO was known to have a significant influence on the Fe-S miscibility gap (*e.g.*, Vogel and Fülling, 1948). This mitigation would have to be rather efficient, because oxygen, too, could not have been present at more than ~1 wt. %.

I had had a similar problem when I first started working in metallic systems. Metallic liquids do not quench to glasses, except with great difficulty, and it concerned me that there might be an immiscible liquid amongst the spray of quench dendrites that I might not recognise as such. Therefore, I set out to “unambiguously” produce immiscible liquids. (Parenthetically, this study later served me well when working in immiscible silicate and immiscible carbonate-silicate systems (Dickinson and Jones, 1989; Jones *et al.*, 1995b)).



One of these experiments gave credence to the oxygen hypothesis. We took an Fe-Ni-S-P composition that had not formed immiscible liquids (but should have), which had been run in a sealed silica tube. We then ran that same composition for a short time, at the same temperature, under flowing H₂-Ar. The experiment was kept short to avoid losing S to volatilisation. And even though we did lose some S, we did form immiscible liquids. So the theory was that H₂ gobbled up the oxygen in the system, thereby promoting immiscibility (Malvin *et al.*, 1986). Still, it is not proven that oxygen was the root cause of Nancy's problems or mine.

9.1.2 Parameterisations in metallic systems

At one point, Nancy went back to the roots of the Jones-Malvin parameterisation and decided it needed a tune-up (Chabot and Jones, 2003).

First, Nancy noticed that the α term could perhaps be dispensed with if the X_S term in equation (5.1) were replaced by a possibly more appropriate algebra:

$$\ln {}^iD = \ln {}^iD_o - \beta_1 \ln [(1 - 2X_S)/(1 - X_S)] \quad (9.1)$$

This translated the model from the sulphur content of the liquid to the siderophile domains of the liquid – a speciation *vs.* a compositional model. For Ir partitioning Nancy found that this renormalisation could remove the α term from equation (5.1). Further, using this parameterisation, a single β could be used for ${}^{Ir}D_{sol\ met/liq\ met}$ in both the Fe-Ni-S and Fe-Ni-P systems. In the Jones and Malvin parameterisation, different β parameters would have been needed for these two systems.

A corollary of Nancy's hypothesis was that more complex systems could be parameterised thus:

$$\ln {}^iD = \ln {}^iD_o - \beta_1 \ln [(1 - 2X_S - 3X_P - 3X_C)/(1 - X_S - 2X_P - 2X_C)] \quad (9.2)$$

This hopeful parameterisation has been both successful and unsuccessful. Even in the original Chabot and Jones (2003) paper, there were elements that could not be fitted in this manner.

There are possibly two reasons for these results. First, the success of fitting ${}^{Ir}D$ probably relates to the avoidance principle of the original Jones and Malvin model – Ir desperately wants to avoid non-metals. But other “siderophiles” such as Ni and Au may partition between siderophile and non-siderophile domains in the metallic liquid. Therefore, Nancy's model works best for elements like Ir and less well for elements that are more ambivalent in their siderophile tendencies.

Second, for non-metals such as P and C, it is uncertain that we know the melt speciation of their compounds. Species such as Fe₂C and Fe₂P are certainly possible and this may complicate the parameterisation process. The assumed speciations in equation (9.2) for C and P are Fe₃C and Fe₃P, respectively. However,



this assumption may not be correct, and, in addition, there may not be a single C or P species in these liquids. So elements such as Au might partition between multiple speciation sites.

Still, other authors have found Nancy's parameterisations useful (*e.g.*, Albarède *et al.*, 2013).

9.1.3 Henry's law

I hope, by this point, readers will consider the issue of Henry's law to be mostly settled in silicate systems. However, John Wasson (UCLA; Wasson, 1999) raised the same Henry's law issue for metallic systems, because much of the experimental data had come from percent-level doping experiments.

Chabot *et al.* (2003) used trace-level doping and LA-ICPMS to dispel this concern. The agreement between percent-level doping experiments and those that were doped at the ~100 ppm level was impressive. It appears that percent-level doping is within the Henry's law region for most siderophile elements in metallic systems.

9.1.4 Partitioning at high pressure

One of my projects with Dave Walker was to see how pressure affected solid metal-liquid metal partitioning (Jones and Walker, 1991b). Initially, I did some piston-cylinder experiments at ~10-30 kbar that showed no noticeable difference from one bar experiments. But Dave was thinking larger, and he put together a multi-anvil cell to do an ~80 kbar experiment.

Things suddenly became tricky. My recollection is that this was the first time Dave had performed a "high-temperature" experiment in his multi-anvil. By "high-temperature," I mean above 1200 °C; and Dave was concerned about this. His newly-invented multi-anvil had no cooling system, and he was worried that the steel anvils that compressed the inner WC truncated-cubes might lose their temper at high temperature. So we were to monitor the experiment closely for signs that things were going wrong.

Things did go wrong, but not experimentally. The next morning, Dave brought the sample up to temperature but then had to quickly leave town for a family emergency. I was left to watch the experiment, which I did. I was watching less like an experimentalist and more like a mother hen, knowing that I had no real idea of what I was doing. But if nothing obvious had gone wrong by the end of the day, I was to cut power and quench. The result was a successful ~8 hour experiment (which may have been a record duration for that era), though even this experiment showed little, if any, pressure effects.



Our rationalisation for such little change in D (compared to silicate systems) was that metals and metallic liquids were such close-packed structures that they had very small compressibilities. Therefore, the pressure difference between one bar and 80 kbar was of little matter to a metal. This is in contrast to silicate systems where compressibilities can be significant.

Nancy decided to re-enter the high-pressure partitioning arena by doing 90 kbar multi-anvil experiments at UNM, where she had connections with Carl Agee and Dave Draper (who had both moved from JSC to UNM). But instead of the ~4 tracer elements used by Jones and Walker (1991b), she had doped with 21 trace elements to analyse by LA-ICPMS and to look for any systematic regularities.

And the regularities appeared (Chabot *et al.*, 2011). There were clearly progressions across the first-, second-, and third-row transition elements. Relative to one bar, some D's went down and others went up, but there was a clear periodicity that is not yet understood. Also, the small pressure-dependence that Walker and I saw in ⁶⁶Zn appeared to fit within the new data set. The Chabot *et al.* (2011) paper is an important result, but its interpretation is still elusive.

9.2 Dave Lindstrom and Nanonuggets

I'm "apparating" back in time to cover a 1990's topic that I think is best discussed here.

With the renewed interest in the geochemistry community to core formation, spurred somewhat by the Jones and Drake (1986a) paper, it became important to determine the solubility limits of siderophile elements, particularly as a function of oxygen fugacity. I don't remember the details, but Dave Lindstrom roped me into working with him on Ir partitioning experiments that had been performed by Hugh O'Neill in Bayreuth, Germany, and then analysed by Herbert Palme in Mainz, Germany. In Bayreuth, there was a vat of silicate liquid (haplobasalt) in an Ir crucible, that was stirred with an Ir stirrer, and which was periodically sampled over a course of months (O'Neill *et al.*, 1995). The experimental design was elegant, but the results were complicated. The theory was that, as the liquid was stirred, any nuggets would somehow be removed over time. And the analytical results bore this out somewhat.

Lindstrom used his before-mentioned micro-analytical INAA technique to analyse samples a few ten's of micro-grams in size. Iridium is an element that is perhaps best analysed by neutron activation, as opposed to ion probe or ICPMS techniques. Therefore, Dave could analyse multiple samples of a single aliquot of glass. What Dave saw was a tremendous range of Ir concentrations within a single "homogeneous" aliquot. This was hard proof that the nanonuggets existed. And some simple diffusion modelling further suggested that they did not grow during the quench (Lindstrom and Jones, 1996).



The nanonugget issue is still with us (but see below). However, one advantage of LA-ICPMS is that nuggets are detectable by looking for spikes in the concentration signal, as the laser ablates deeper into the charge. The hope is that analyses that cluster around a single, low value yield the true siderophile element solubility. Conversely, it may only mean that we are measuring a dispersion of even smaller nuggets.

9.3 Valerie Malavergne and Pt Partitioning

In a collaboration on martian siderophiles with Clive Neal (Notre Dame University), we reviewed what was known at the time (Jones *et al.*, 2003). We noticed that, compared to most other highly siderophile elements (HSEs), Pt was rather invariant. This led to the surmise that bulk ^{Pt}D must be about unity for martian basalts (Fig. 9.1). A further review of Pt in lunar mare basalts and terrestrial komatiites turned up scant data, but the existing data seemed to support this idea. Martian basalts are simpler than terrestrial basalts, with respect to siderophile elements, because they appear to have rarely experienced sulphide liquid immiscibility. Because of this, shergottite HSEs have regular fractionation patterns that correlate with lithophile elements (Jones *et al.*, 2003). With the exception of komatiites, this is not generally true of terrestrial basalts. Most terrestrial basalts have segregated an immiscible Fe-S liquid and lost siderophiles in the process.

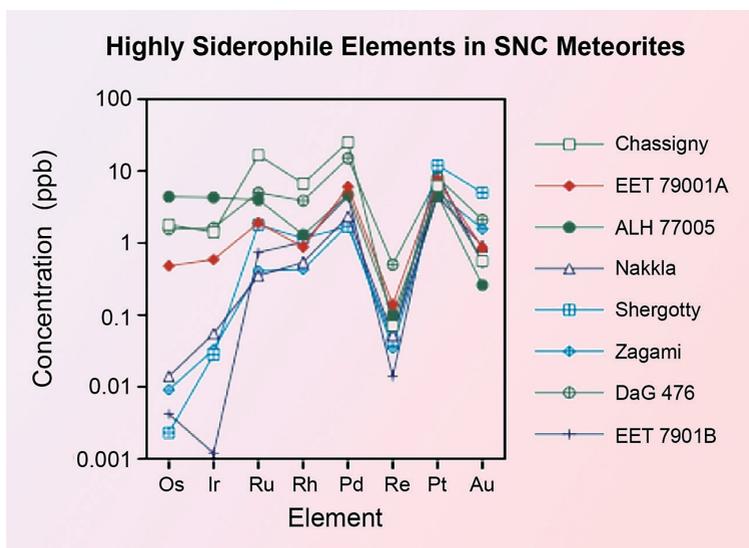


Figure 9.1

Concentrations of highly siderophile elements (HSE) in martian meteorites. Note the tight clustering of Pt analyses (3-10 ppb) compared to the other HSE. Data from Jones *et al.* (2003).



Not long after this, I received a surprise letter from Valerie Malavergne (Université Marne la Vallée), who would be spending a year or two in Houston. She wanted to do experiments, and based on my earlier speculations, it seemed interesting to look at Pt partitioning into olivine. Onuma diagram considerations also suggested that Pt^{2+} might be quite compatible in the olivine structure (Jones *et al.*, 2007). Valerie then became a visiting scientist at the local LPI.

This adventure turned out to be quite a flop, but through no fault of Valerie's. I had given her a bad project – a bum steer. In addition, we had to rely on others to analyse Valerie's experiments. One of these, Andy Campbell, remarked that he had analysed siderophile-element partitioning experiments for a number of people and that these were the best he had ever seen, as judged by nugget spikes in the LA-ICPMS signal. Despite that, he really couldn't detect Pt in our experimental olivines. *C'est la vie*.

Valerie was not exactly a geochemist; she was really a physicist. However, as Andy (University of Chicago) can attest, she learned experimental techniques very quickly. Our siderophile element dopant was a mixture of Pt, Au, Pd, and Ru. For the first three elements at least, we chose them because it seemed that they were less likely to form nanonuggets, based on reports from other experimental groups. I suspect the inspiration for this largely came from papers by Alex Borisov. With hindsight, this choice appears to have been correct.

Our capsules were San Carlos olivine (peridot) and Valerie learned to drill capsule holes in them, using advice from Steve Mackwell, the LPI director. He advised drilling while the peridot was under water, so that thermal stresses would not crack the crystal. And, afterward, it was very easy to tell the experimental olivines from the capsule olivine because of the large difference in FeO content. But despite all these experimental successes, the project was a bust. ☹

What could have gone wrong? Martian basalts showed comparatively little variation in Pt concentrations and an Onuma 2+ ion diagram predicted that Pt^{2+} (the expected valence) would have a $D_{\text{ol/liq}}$ of near unity.

The reasons for this failure appear to be rooted in crystal field theory. Although we seldom think about them in terms of crystal-field geochemistry, the lower-row transition elements are believed to be more susceptible to crystal-field effects than even the first-row transition elements because of their larger size (Jones *et al.*, 2007). And Pt^{2+} prefers not to be in octahedral coordination (Greenwood and Earnshaw, 1984). The reason that Pt is so invariant in martian basalts is still unknown. Regardless, it appears that the Onuma diagram prediction, with the assumption that Pt^{2+} would wish to partition into an octahedral site, was, indeed, a bum steer. Therefore, I owe Valerie an apology. I should have offered her a better project.



10.1 Ni Metal Solubility in Silicate Liquids

Ehlers *et al.* (1992) proposed the possibility that, at normal magmatic temperatures and low oxygen fugacities ($\sim IW$), a significant proportion of Ni in the silicate liquid existed in the zero-valent state, *i.e.* metallic Ni. Subsequently, Colson (1992) performed Ni solubility experiments in very reducing systems and reached a similar conclusion.

There must be an explanation for the Ehlers experiments; I do not believe these were bad experiments. Therefore, more experiments and analyses on this composition might be interesting.

10.2 Pt Metal Solubility in Silicate Liquids and Partitioning at Extreme Temperatures

The issue of zero-valent Ni has been doubled-down on with respect to Pt. Despite being a co-author on a paper advocating metal solubility in silicate liquids (Walker *et al.*, 1993), I was never a true believer. Rama Murthy's model of metal-silicate equilibrium resonated with Walker but not with me. I think I did make some analytical contributions to that paper, but I was not convinced as to its main conclusions. Elemental trends seemed to indicate mixing between silicate and immiscible metallic liquids (*i.e.* a nugget effect). I argued for such, but in the end, the first author gets the final say.

However, a later paper by Cottrell and Walker (2006) was more persuasive. Furthermore, other authors (*e.g.*, Li and Agee, 1996; Righter *et al.*, 2008) believe that the HSE abundances in the Earth's mantle may be understood in terms of high-temperature, high-pressure equilibration with metal.

In terms of the Cottrell and Walker (2006) and Walker *et al.* (1993) papers, the temperatures of these experiments were as different from those of ordinary igneous temperatures as volcanic temperatures are from room temperature. Therefore, our current igneous experiences may not serve us well above 2000 °C.

In this context, it is interesting to contrast two very different sets of studies of the solubility of Pt in silicate liquids:

- (i) The low-pressure, high- f_{O_2} , igneous-temperature experiments of Borisov and Palme (1997) and Ertel *et al.* (1999) indicate that Pt behaves as Pt^{2+} above the Ni-NiO oxygen buffer. Below that buffer,



the Pt composition of the liquid remained constant and the inference was that nuggets had formed at reducing conditions and that the melt was effectively saturated in Pt metal.

- (ii) The high-pressure, low- f_{O_2} , igneous-to-extreme-temperature experiments of Bennett *et al.* (2014) and Médard *et al.* (2015) appear to show that Pt exists as some reduced species – as Pt metal or as an inter-metallic compound. These may not be discrete phases, but perhaps exist as true melt components. The opinion of Médard *et al.* is that the solubility of Pt in silicate liquids (and, therefore, the metal-silicate Pt/D) is almost solely dependent upon temperature, but these authors appear not to have included experiments as oxidising as those in category (i) in their temperature regression. But for whatever reason, the Médard *et al.* temperature regression does not fit the Cottrell and Walker (2006) data. This is perhaps because these experiments were the most reducing (~IW-2), but Médard *et al.* argue that f_{O_2} has only a weak effect on Pt solubility.

So almost overnight, the landscape of Pt solubility has apparently changed. Partly, this appears to be due to improved experimental techniques (*e.g.*, the reduced experiments were pre-reduced before the experiment, which seems to have prevented nanonugget formation) and partly due to our ability to now achieve extreme temperatures. These new developments may have some inconsistencies, but they raise interesting possibilities for future research.

Questions that may be asked include:

- (i) Is geochemistry at extreme temperatures rather different from the igneous temperatures to which we are accustomed? For example, if the early Earth were totally(?) melted by a Giant Impact, will our conventional geochemical wisdom be of much use?
- (ii) Is Pt, in reduced, igneous-temperature basaltic liquids, in the 2+ state? If the system is not Pt-saturated, as are the reduced igneous-temperature experiments, this is still a possibility.
- (iii) If the answer to (ii) is “yes,” then can the difference in geochemical behaviour between reduced Pt species and oxidised species be used to evaluate different models of core formation and the differentiation of the early Earth? These are the questions for you, the next generation.

And as a final note on this issue, both Bennett and Médard conclude that their metal/silicate partitioning studies imply the necessity for a late veneer. *Rats!*

10.3 Pt Mineral/Melt Partitioning in Silicate Systems

Despite our inability to persuade Pt to enter the olivine structure, the original observation remains: Pt in shergottites is much less variable than other highly siderophile elements in martian meteorites (~3-10 ppb; Fig. 9.1; Jones *et al.*, 2003);



and there must be a reason for this near-constancy. More-detailed inspection of the shergottite data suggests that the limited Pt variability may correlate with that of a heavy REE, such as Yb, which would be consistent with its apparent compatibility in some phase (Jones *et al.*, 2007). But as mentioned above, the relatively high concentrations of HSEs in shergottites suggest that metal/sulphide fractionation was not a factor.

In principle, this is an issue of some importance. A set of well-defined PtD 's would be extremely useful for determining its abundance (and possibly the abundances of other HSEs) in planetary mantles. This, in turn, has bearing on the earliest accretion and differentiation processes in the inner solar system.

In practice, however, the next step is not so clear, especially in light of the preceding section. Since we are concerned with (at least) the shergottites and Mars, silicate perovskite cannot be a solution to this problem (pressures in Mars are too low) – nor presumably are other candidate minerals with octahedral cation sites, such as pyroxenes. Other mineralogical possibilities are garnet, which has an 8-fold coordination site for 2+ ions, and spinels, which have tetrahedrally coordinated 2+ sites.

Several studies have shown that fractionations of the shergottite Sm-Nd chronometer system appear to require garnet in the source region (*e.g.*, Jones, 2015). Therefore, shergottite melting appears to have been at pressures higher than the stability field of magnesian spinel ($MgAl_2O_4$). So if magnesian spinel is involved in shergottite Pt geochemistry, the connection is currently unclear. And, by itself, spinel as a host for Pt would not explain the correlation with HREE.

A final possibility is that Pt^{2+} partitions into the tetrahedral site of chromite. Because of CFSE effects, Cr^{3+} may gobble up all the octahedral sites in chromite, so that 2+ ions are all relegated to the tetrahedral site (O'Neill and Navrotsky, 1984). A problem with this suggestion is that the ionic radius of Pt^{2+} is possibly too large to fit into the tetrahedral chromite site that it prefers. But, at least in octahedral coordination, the ionic radius of Pt^{2+} is not that different from that of Fe^{2+} (Jones *et al.*, 2007). Therefore, perhaps we should consider the possibility that chromite partially buffers the Pt concentrations of martian basalts. That said, Brenan *et al.* (2012) saw no tendency for Pt compatibility in chromite.

10.4 Compatibility of Ir and Os

Iridium and Os have very similar geochemical tendencies, and our experience is that, for Mars, both Ir and Os behave compatibly during mantle partial melting, as well as during fractional crystallisation (*e.g.*, Jones *et al.*, 2003). For the Earth, the geochemistry of Ir and Os is not well understood – at least partially because most terrestrial basalts (*i.e.* MORB) have apparently experienced sulphide-liquid immiscibility (*e.g.*, Rehkämper *et al.*, 1999). This late-stage process will overprint behaviours that may have occurred before. Regardless, many observations indicate that both Ir and Os act as compatible elements during basalt petrogenesis.



Analyses of the martian shergottite meteorites appear to be better indicators of Ir and Os behaviour than are analyses of most terrestrial basalts. First, these basalts show no sign of sulphide liquid immiscibility. This is primarily because the shergottites are both more reduced than most terrestrial basalts and also have higher FeO contents. Both low f_{O_2} and elevated FeO discourage the formation of Fe-S immiscible liquids. Secondly, the relatively high abundances of HSE in shergottites also argue against removal by sulphide-liquid immiscibility. Once an Fe-S liquid appears, the concentrations of HSE's in the silicate portion of the system drop precipitously. Thirdly, Jones *et al.* (2003) have shown that shergottite Ir and Os concentrations are correlated with MgO, a lithophile element.

But the bottom line is that the host for Ir and Os, when they act as compatible elements in silicate systems, is not well known, although Righter *et al.* (2004) and Brenan *et al.* (2012) report that $^{187}\text{D}_{\text{chromite/liquid}}$ can be very large.

10.5 Theoretical Basis for Crystal Field Effects

I once mentioned to my thesis advisor that there must be a problem with crystal field theory. It involves a d-d transition, which we all learned in freshman chemistry is forbidden. He looked slightly startled, but said, "You're right." I don't think he had thought about this complication before. I know I hadn't.

This should not have been news to me. Early in Roger Burns' 1970 book, he states categorically that this is a forbidden transition. There is no change in the quantum angular momentum parameter (l) in s-to-s, p-to-p, or d-to-d, etc. transitions. But photons have angular momentum of unity and that angular momentum must go somewhere. So I asked another professor if the spin of the electron is flipped during a d-d transition. That could explain the lack of a Δl if the spin went from $-1/2$ to $+1/2$. But the answer I got was, "No".

I don't know if this observation has any importance. Probably the answer is that the dominantly d orbitals are actually hybrids. But it's possible that there is some real science involved with this issue. And it's also possible that the answer is already known, just not to me.

10.6 U-Th-Series Disequilibria

Very sophisticated models have been proposed to understand the fractionation of short-lived elements in the decay chains of U and Th. My personal view is that these models may be too petrologically simplistic. The porosities (*i.e.* degrees of partial melting in my over-simplified way of thinking) that have been proposed in these models ($\sim 10^{-3}$ - 10^{-4}) are so low that it is not clear whether they are physically realistic in low-FeO terrestrial systems. Low-degree silicate melts tend to be silica- and alkali-rich and these melt compositions usually have high viscosities. In order for such low-degree melts to be mobile enough to escape their source regions, they may need to be either water- or CO_2 -rich (or both).



A real question is whether the suggested mineral controls on these fractionations have any major effect. The modelled minerals are typically modally abundant minerals – Ca-rich pyroxene and garnet. If porosities of 0.1-0.01 % are required to produce the required fractionations, it is not clear whether major minerals have real influence. Minor minerals such as phosphates and iron oxides may be the controlling factors. Other trace minerals may be even more important. If predicted porosities were ~10 %, then most minor and trace minerals should have been dissolved and only major minerals should control U-Th chain partitioning.

John Longhi (pers. comm.) has countered this argument by noting that (for example) phosphates are not predicted to be liquidus phases for basalts, based on phase equilibria calculations. But a low-degree partial melt that has an established trace-element signature may later, through transport to the surface, sufficiently assimilate mafic minerals such that the criterion of phosphate saturation is lost via mafic mineral reactions (*e.g.*, polybaric melting). Therefore, dilution of P by polybaric melting may have removed phosphate from the liquidus, while retaining the trace-element signature.

I have not kept up with this field, so what I've written here may be terribly out of date. Still, I think it would be worthwhile to further study the partitioning behaviours and diffusivities of members of the U-Th decay chain, and to study minerals that may be minor or trace phases in the upper mantle. The calculated porosities are determined through knowledge of partition coefficients. Porosities of 10^{-3} - 10^{-4} are deemed necessary because those are thought commensurate with measured partition coefficients. However, a simplistic (and perhaps extreme) example is that a porosity of 10^{-2} might provide adequate Th/U fractionation if there were a mantle phase that had a modal abundance of 0.1% and a $^{238}\text{U}/^{232}\text{Th}$ of ~10.

10.7 Origin of Martian and Lunar Basalts

Several authors have attempted to model lunar and martian basalts in terms of the Sm/Nd and Lu/Hf fractionations that occurred during their petrogenesis (*e.g.*, Beard *et al.*, 1998; Blichert-Toft *et al.*, 1999; Shih *et al.*, 2010; Jones, 2015). All of these studies have concluded that extremely small degrees of silicate partial melting must occur in the presence of garnet. These degrees of partial melting may be more physically reasonable than those alluded to just above, in the discussion of U-Th series disequilibrium, because the FeO contents of lunar and martian basalts are so much larger than those of terrestrial basalts. FeO acts as a network modifier in basalts and, thus, lowers the viscosity of basaltic melts. Lunar mare basalts, martian shergottites, and eucrites all have ~2.5 times more FeO than terrestrial MORB or OIB. Therefore, removing a very small-degree partial melt from these extraterrestrial source regions may perhaps be easier than on Earth.



Still, these estimates of partial melting are models based on experimental partition coefficients, and the bulk of the experimental partition coefficient data is most relevant to terrestrial, FeO-poor compositions. And at least in the case of garnet, Draper *et al.* (2003) have shown that REE partitioning in FeO-rich systems does not behave the same as in terrestrial systems. Therefore, there is some uncertainty in these calculations, and it would be helpful to have a partitioning data set that is known to be applicable to planetary, FeO-rich systems.



In my introduction, I said that this submission was meant with grad-students in mind. Therefore, it seems appropriate to end this paper on those terms.

11.1 General Advice

I much admire a short work entitled “Advice to a Young Scientist” (Medawar, 1979), which appears to still be available from Amazon. Except for the fact that he assumed everyone exclusively published in *Nature*, I believe Medawar offers much wisdom. And considering the fact that Medawar was a Nobel Laureate, one might conclude that he knew of what he spoke. He also wrote well. One of his better turns of phrases was that students should avoid those professors who “*are well known habitually to eat their young*”.

I would also say that there is a very fine line between choosing a graduate school that makes you comfortable and one that challenges you. In my own case, I can’t honestly say that I enjoyed my grad-school experience, but I did learn a lot. That said, different universities have different educational philosophies. And I think that it is advantageous to choose a school whose philosophy will not hinder you. Frankly, this is difficult to know in advance. I think I finally understood some major philosophical contrasts between myself and my graduate school, but only a decade or so after graduation.

One personal example is that I am more of a generalist than a specialist. My grad-school emphasised just the opposite. There are important niches for both these types of scientists, but I chose a grad-school that was not particularly supportive of people who were not specialists. With hindsight, that was a problem. But my later experience has been that it is easier for a specialist to arrive at the wrong conclusion than for a generalist. In the end, all the pieces of the jig-saw puzzle must fit.

So, in choosing a grad-school, there is a tension between finding a compatible academic philosophy and the adage that “*what doesn’t kill you, makes you stronger.*”

I believe this choosing is easier now than when I was a prospective student. Grad-schools now routinely invite students, to whom they have made offers, to their campuses. In making your decision, you can meet faculty and grad-students; you can also get a feel and flavour for the school and the department. I believe this is an important experience and should be encouraged – especially talking to the grad-students.



11.2 Is Grad-School Right For You?

A reviewer of this paper has made the suggestion that I should address whether grad-school should be a person's first option. This is a wise comment. I think that many bright people find academic life easy and then follow the easiest path – grad-school. But there is a tendency for those people to wake up one day, discover that they are forty years old, and wonder if they have wasted their lives. My personal explanation for this phenomenon is that these people had never learned what they really didn't want to do.

In my own case, I can cite several examples of things that I learned I did not like to do: mowing yards, digging potatoes, hoeing cornrows, military marching, and listening to droning on subjects I care nothing about. So my advice is to take some time to discover what you hate doing before you take the easiest path. Get some experience outside of academia.

But a fundamental bottom line is that grad-school is hard. Therefore, if you are not deeply committed to this path, you should think twice.

11.3 The Double Helix

A book that I have enjoyed and think is very educational is *The Double Helix* (Watson, 1968). Some people philosophically hate this book. My personal opinion is that it portrays a very honest account of how science is actually done – warts and all. The science of the book is compelling. But it is undeniable that another major theme is that of scientific competition.

There is virtue in honesty, even if not all the stories are flattering. But, as in the case of Medawar, when Nobel Laureates allow you to peek inside their heads, I believe you should be grateful. Somehow, they did something right.

11.4 Personal Confidence

In the scientific world, there is a very fine distinction between being confident, over-confident, and arrogant. I believe that, in order to be a good scientist, self-confidence is not a luxury – it is a requirement. As Mark Twain is reported to have said, "*A man cannot be comfortable without his own approval.*" In my own case, by the time I got my Ph.D., my confidence level was rather low. Since then, my self-esteem has increased somewhat. But my advice is that confidence is only truly achieved by personal accomplishments – not by demeaning others or from the praise of colleagues. I will say that the latter is very gratifying, but you should not expect others to raise your own self-esteem. That's your job, through your own successes.

Happy trails!

(Rogers and Evans, 1952; <https://www.youtube.com/watch?v=HMqXdrUjEe8>)



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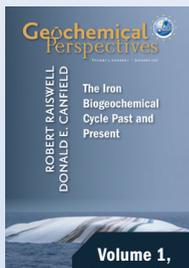
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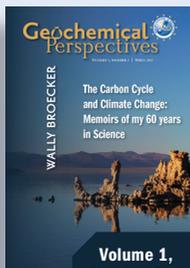
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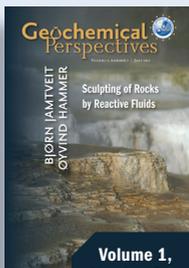
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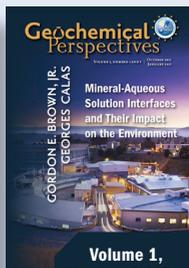
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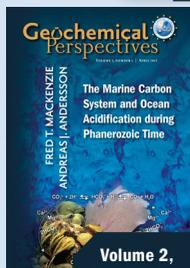
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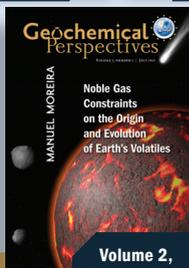
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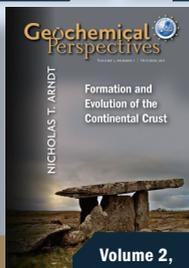
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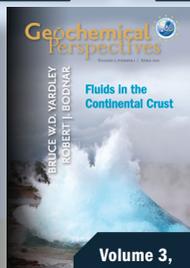
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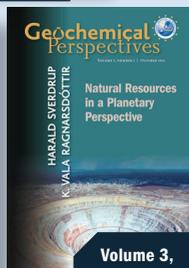
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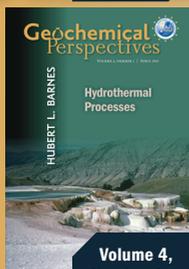


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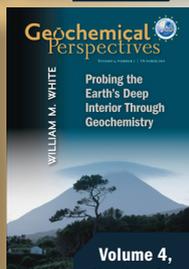


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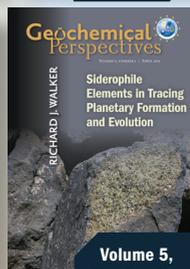
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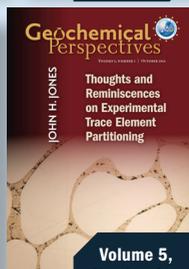
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John has broad interests in planetary geochemistry: Origin of the planets and planetoids of the inner solar system, core formation, the early evolution of planetary atmospheres, origin of planetary basalts, parameterisation of experimental partition coefficients, nuclear processes as applied to geologic problems, and experimental geochemistry and petrology.

John was born in Kentucky (USA) and grew up in a small town of about 200 people. Inexplicably, this town has produced three Ph.D.'s: one in analytical chemistry, one in geochemistry, and one in political science. The town's main claim to fame, though, is that Peewee Reese, a long-time shortstop for the Brooklyn Dodgers baseball team, was born just outside the city limits.

John is a Fellow of the Meteoritical Society and the Mineralogical Society of America. He is also a member of the American Geophysical Union and the Geochemical Society. He has co-edited two books and published over eighty papers. He has served on several NASA panels and committees of professional societies. He is currently a member of the SAM instrument team, a part of NASA's Curiosity Rover mission that is exploring Gale Crater on Mars.