

Geochemical Perspectives

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HUBERT L. BARNES

Hydrothermal Processes



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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ABOUT THE COVER

Terraces of hydrothermally deposited travertine (CaCO_3) in Mammoth Hot Springs of Yellowstone National Park, northwestern Wyoming. Typical temperatures of the solutions in the springs are below boiling, typically about 80 °C.



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FOREWORD

I initially got to know about *Hu Barnes'* work in the mid nineties while a PhD student at ETH Zürich and as I read the 2nd edition of "Geochemistry of Hydrothermal Ore Deposits". The various chapters in that book taught me that *Hu* and his collaborators have in many ways throughout the latter part of the 20th century revolutionised experimental hydrothermal ore deposit geochemistry and helped us better understand how our planet's ore deposits formed. I wanted to learn from that.

What is my real link to *Hu*? While doing an experimental PhD with *Terry Seward* (see Section 3.1) I realised that the other person whom I absolutely wanted to work with in order to learn as much as possible about experimental approaches was *Hu*. I wanted to mine his vast knowledge of experimental tricks and naturally work with another 'legend'. Thus I joined him at Penn State for a 3 year postdoc and what a ride it was. I had brought with me from Zürich the *laissez-faire* and interpersonal humour from *Terry's* group and after the initial shock in the more conservative Ore Deposit Group at Penn State I discovered that *Hu* was not (contrary to what most people still think) a grumpy old man but that he was actually a fun person, not just to work with but also to spend time with. I know many people will find this surprising but under the 'grumpy' old man, there is a gem hidden. Among the many memories I cherish is a canoeing trip down the Allegheny River with him and his wife *Mary* and the very memorable excursion to Kamchatka (see picture of *Hu* on back cover) after the Water Rock Interaction 8 meeting in Russia. There, *Hu* was one of the few who made it up all the way to the top of Mutnovsky volcano and he was 72 years old at the time. I knew I



wanted to (at least in part) become like him. During my tenure at Penn State as one of his last 2 postdocs (*Rick Wilkin*, now at EPA being the other one) I was in awe because above the door of our office were the name tags of so many of the great scientists in geochemistry and they all had worked with *Hu* at Penn State. It was big shoes to step into but naturally I did not only learn hydrothermal experimental tricks from *Hu* but also many research life tricks that have served me well over the years. *Hu* and I have kept in touch since I left Penn State; these memories as well as *Hu's* many achievements and contributions convinced me that I had to persuade him to write an issue for *Geochemical Perspectives*. I wanted him to describe *his geochemical story* for the future generations. I also wanted the publication of this *Geochemical Perspectives* to coincide with the 25th anniversary of the annual Goldschmidt Conferences in Prague because *Hu* was more than just instrumental in initiating this conference series (see Section 7).

I very much enjoyed editing this with *Hu* and I hope you enjoy reading it.

Liane G. Benning

Geochemical Perspectives Editor



ACKNOWLEDGEMENTS

I very much appreciated many editorial suggestions that resulted in valuable revisions to the manuscript of this issue of *Geochemical Perspectives*. Extensive editing was contributed by *Liane G. Benning*, University of Leeds and now at the Geoforschungs Zentrum in Potsdam, and *Dave Wesolowski*, U.S. Oak Ridge National Laboratory. Sections were reviewed by *Martin Schoonen*, U.S. Brookhaven National Laboratory; *Terry Seward*, Victoria University, Wellington, New Zealand; *Antonio Lasaga*; *Roger McLimans*, DuPont Corporation; *Jim Murowchick*, University of Missouri-Kansas City and *Mary Barnes*, Penn State University.

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HYDROTHERMAL PROCESSES: THE DEVELOPMENT OF GEOCHEMICAL CONCEPTS IN THE LATTER HALF OF THE TWENTIETH CENTURY

ABSTRACT

This *Geochemical Perspectives* follows along my path through the evolution and development of hydrothermal concepts as they became established during the latter half of the twentieth century, from conjecture through established precept. A powerful stimulus for the developments was a keen scientific interest in the genesis of hydrothermal ore deposits shared commonly by my colleagues, both geochemists and economic geologists. Underlying that interest was our optimistic belief that a fundamental understanding of ore-forming processes should have practical applications for mineral exploration.

Our early investigations of ore genesis were impeded, however, by a lack of adequate data on the chemistry of aqueous solutions at the high temperatures and pressures of hydrothermal processes. Even the prime parameters used typically by physical chemists to quantify acidity and oxidation state of solutions at elevated conditions were awkward. Instead, we soon adopted both the ionisation constants of nature's common brine solutes in order to evaluate acidity, as well as oxygen fugacity to index the oxidation state of hydrothermal fluids.



Furthermore, we found that information on the high P-T volumetric and thermodynamic behaviour of volatiles like CO₂, CH₄, H₂S, SO₂, and especially H₂O were incomplete for applications which ideally extend to about 1,000°C and 10,000 bars. This resulted in extensive experimental investigations internationally by geochemical laboratories that painstakingly provided much of the fundamental new data still currently used.

That crucial, advanced chemical information could be applied effectively only if the physical conditions (P, T) of the environments where ores had formed were more accurately identified. To better resolve these temperatures and pressures, a series of geothermometers and geobarometers were invented and tested on various settings. Two of these, the quartz geothermometer and the sphalerite (ZnS) geobarometer, are special in that they are flexibly adaptable to a variety of mineral deposits. Their attributes favour relatively easy application so I have selected them for a more thorough examination. Another family of highly useful geothermometers are dependent upon the unique characteristics of the ubiquitous iron sulphides. There are more than seven of these sulphides and most ore deposits contain more than one of them. These sulphides are especially important as precise indicators of the environmental conditions where they crystallised, not only due to their occurrence within a deposit but also by differences in their solid solution composition and in morphology. We found that variations among the characteristics of the iron sulphides were largest precisely within the range of conditions of chemistry, temperature, and pressure where ores crystallise, attributes which made these indicators extremely valuable.

The nature of hydrothermal processes found from the rock record through mineralogical evidence on ore deposits was naturally supplemented by data from investigations of modern and active geothermal systems. Our initial consideration was to ascertain whether geothermal processes and hydrothermal ore genesis were related phenomena. In fact, it turned out that their ranges of temperatures and pressures and their deduced lifetimes were identical. Therefore, the measured solution flow rates and compositions of modern geothermal systems provided excellent baselines for modelling what must have transpired in ore-forming environments, which are simply ancient geothermal sites.

Having established the physical conditions and processes that characterise hydrothermal environments, our next problem was to determine the means of aqueous transport and how fluids could have caused ore-grade mineral deposition. It was clear that both transport and precipitation depended on the solubilities of ores in reducing fluids at near neutral acidity. In addition, the concentrations of the metals are controlled in such solutions by complexing (bonding) mostly with halide or sulphur-rich ligands. Yet, the stoichiometries (composition ratios) of each of the dissolved metals with these (and other) common ligands had to first be measured. Thus was done by generations of projects around the world and the research has evolved as experimental and theoretical techniques have



continued to provide increased resolution. These techniques and new data sets led to more accurate and precise thermodynamic descriptions of the complexes, which have been used to calculate, and then plot, variations in solubility as a function of oxidation state ($\log a_{\text{O}_2}$) and of pH at pertinent temperatures and pressures. Potential causes of ore deposition are implicit in such diagrams.

The maturity of our understanding of hydrothermal processes could be tested most readily against criteria from the lowest temperature and pressure ore deposits, the Mississippi Valley type zinc-lead ores. The extensive database for those in Illinois, Iowa and Wisconsin made that district ideal as a model. There, the ore-depositing solutions arrived about 270 million years ago from their source in the contemporaneously uplifted southern Appalachian Mountains. They flowed northward through the Illinois Basin becoming heated, highly saline, with a reduced oxidation state, slightly alkaline to neutral acidity, and with solute concentrations apparently especially rich in iron, barium, zinc, and lead. It was effectively a hot groundwater that flowed at about 11 metres per year from its source for 1100 km to the district to precipitate sulphides within an horizontal 35 metre depth range about 1 km deep. The mineral paragenetic sequence revealed that slight oxidation was sufficient to cause sulphide deposition dominantly at $125 \pm 25^\circ\text{C}$ and for sphalerite (ZnS) at a yearly rate of coating of about $0.2 \mu\text{m}$. Four independent methods agreed that the process continued for about 0.25 million years. However, the aqueous complexes have not yet been identified for certain. Those metal-carrying aqueous species must have provided sufficient solubility to form deposits over an area of 10,000 square kilometres. Because the very regular banding in sphalerite could be correlated over a very large area implies that there must have been continuing, recycling climate control of that ore-forming hydrothermal system. This observation is intriguing and still unresolved and calls for additional studies and a mechanistic explanation.

The development of this field is naturally as you will see closely intertwined with me and my colleagues' research over the last 6 decades and what a journey it was. I hope this *Geochemical Perspectives* gives you, the reader, an insight into one such journey. Mine. Enjoy!



1.1 My Personal Journey

In this *Perspective* of the evolution of hydrothermal concepts during the last half of the twentieth century, my (Fig. 1.1) purpose is to provide an overview of how the field developed and the consequences to my life especially through extensive collaboration with colleagues over the five decades. Far more detailed technical discussions of many of the concepts can be found in the three progressive editions of *Geochemistry of Hydrothermal Ore Deposits* published in 1967, 1979, and 1997, that cover a span of three decades of our slowly developing comprehension of ore formation.



Figure 1.1 Hu Barnes.

While preparing this *Geochemical Perspectives*, a compelling conclusion became evident, that the nature and capabilities of colleagues are crucial to the evolution of a career. They provide stimulation and advice on discovering and evaluating opportunities at each juncture in life.

At Lexington, Massachusetts High School in the 1940's, welcome distractions were sports, for me especially in track and football. My friend *Bernard Burke* (Fig. 1.2) was a compatriot who was active in the same sports and also in playing the violin. He had additional virtues that gradually became more appreciated. His father, a math teacher at Rindge Technical High School, continued to challenge *Bernard* intellectually. The stimulus was contagious as we became competitors academically and companions in the social activities at school and in weekend violin and composing lessons at the South End Music School. Those



Figure 1.2 Bernard Burke.

Courtesy of M.I.T. Kavli Institute for Astrophysics and Space Research.

happy lessons led to considering music as a profession but a new violinist at the Music School became proficient with Beethoven's violin concerto in only two years, way beyond my multi-year competence. *Bernard* and I both concluded that science was equally entertaining and that in nearby Cambridge, the Massachusetts Institute of Technology (M.I.T.) might be the route to interesting lives maybe as wealthy consultants. That dream led through undergraduate years at M.I.T. However, instead of following our financial inclinations, we both



became research-oriented, *Bernard* eventually as William A.M. Burden Professor of Astrophysics at M.I.T. and I as Distinguished Professor of Geochemistry at Penn State. My route there was the product of successive optimised choices.

The students entering M.I.T. with us in 1946 were predominantly veterans returning from World War II. They carried experiences that often gave academic advantages unusual for entering students, even to that Institution. Their level of performance meant that green high school students faced an intellectual transition that overwhelmed some quite intelligent colleagues who sadly gave up and transferred. The more stubborn types gradually adjusted to the time and performance demands, eventually to our benefit. Like *Bernard*, my major initially was physics. That field seemed to be fairly prosaic compared to an elective course in geomorphology taught by *Prof. F.K. Morris*. His skill with coloured chalk gave us picturesque landscapes on the room's three blackboards by the end of each period. The class, mostly of taciturn veterans, often applauded spontaneously at the conclusion of his lectures. His stories of geologic mapping in the wilds of Outer Mongolia added to the conviction that I should change majors to geology. My addiction to rock climbing and camping reinforced that choice and added to the inducement of probable exotic travel.

In the meantime, a job provided some income, ten hours per week as a technician in the Biology Department of M.I.T. There the principal effort was constructing, in a superb machine shop, the stainless steel body of one of the initial artificial kidneys under the direction of *Prof. D.F. Waugh*. Those were long days. Besides that employment were normal lectures, interminable homework plus commuting with buses and subway to M.I.T. which consumed the available hours but taught a capability of lifelong value – going to sleep whenever no action was required. For example, while standing in a subway car and holding onto its passenger hand straps, dozing was automatic. Sleep often arrived but ended sometimes with consternation by falling onto the lap of someone lucky enough to have captured a rare empty seat.

Recreation for us geology students often was centred on the M.I.T. Outing Club for fun and with valuable consequences. The senior members of the Club passed on to us neophytes their expertise with rock climbing and skiing, both nice diversions and also useful for field work. We learned at the Quincy, Massachusetts Quarry to rappel and to use climbing techniques and equipment from the Club's inventory. That capability opened for the future possibilities for rock sampling and mapping of terrain that was otherwise inaccessible. Also, having both coaching and rental equipment available through the Club meant learning to ski was optimised. For me, that ability found use much later during Newfoundland mineral exploration where access was less difficult over ice and snow cover. It also allowed wintertime sampling of volcanic springs and lakes of the Japanese Alps with *Prof. Boku Takano* of the University of Tokyo. Our purpose was to analyse for thiosulphate and polythionate concentrations as indicators of the imminence of volcanic activity (Takano *et al.*, 1984, 1994).



An example of an Outing Club-stimulated activity was a particular mid-winter tour during the 1948 term break by three sophomore geology majors: *Fred Barker* from Seekonk, Massachusetts, *Robert (Bob) Leonard* from Manville, New York, and me from Lexington, Massachusetts. On Thursday, January 29, *Bob* and I left M.I.T. by hitchhiking with the intent of meeting *Fred* at Pinkham Notch, New Hampshire to climb Mount Washington together. Being impecunious students, we minimized our costs by free hitchhiking. *Bob* and I carried army surplus packs containing for each of us two sleeping bags to be nested, spare clothes, flashlights, matches, a canteen, cooking kits, some food and a guidebook. The packs each weighed 80 lbs (36 kg). I wore long johns, wool hunting pants, a Bean's Chamois shirt, a wool mackinaw, and rubber boots. *Bob* had field boots, heavy pants, and a windproof jacket. We both carried crampons and Maine-style, tear-drop-shaped snow shoes about 4.5 feet (1.4 m) long, obtained from an army surplus store at minimal price.

Together with the packs and snowshoes, we made a sizable load so hitchhiking was very slow as most vehicles simply could not take us on board. The consequence was that *Bob* and I covered during the first day only 2/3 of the distance to our goal, Pinkham Notch, and at about dark, gave up and asked at a New Hampshire farmhouse if we could sleep in their garage overnight. Having had no dinner and lying on their concrete floor was not a comfortable night.

Friday morning was snow-free but bitterly cold. Having no alternative, we started hitchhiking soon after daylight. Eventually, a friendly pickup driver offered us a ride if we would load ourselves into the back of his truck. Although that offered no chance for breakfast and it was downright windy and frigid in the back of the truck, we climbed aboard. In a few hours and with successive truck rides, we arrived near mid-day at Pinkham Notch where there was a fresh, deep snow pack.

Our immediate objective was to climb the Fire Trail (now the Tuckerman Trail) up to Hermit Lake Shelter in Tuckerman Ravine where we planned to camp as a base for later climbing, first up Lion Head bluff, then across Alpine Garden, and finally up the top cone of the mountain (Fig. 1.3). However, lack of nourishment, the deep soft snow, the heavy packs, and the awkward snow shoes slowed the hike to a crawl. About half way up the trail, we ran out of energy and had to eat something. The only edible item in our packs not requiring cooking was a package of Dromedary dried dates. Because the package was frozen and our hands were stiff with the cold, we soon found that the only solution was to break the container in half and eat it, dates, cardboard, cellophane and all.

Fred joined us at the Hermit Lake three-sided shelter (Fig. 1.4), having used his skis to negotiate the Fire Trail. The shelter was oriented with an open fourth side toward the mountain to limit the fetch for gusty winds. In the open side was a rough, loose-stone fireplace where smoke from the fire was vented away from the interior. However, the heat produced by rapid burning of dead branches was not enough to have much effect on the shelter's temperature. The fire was crucial to prepare a very much needed hot dinner as quickly as our cold, stiff hands would allow.

That night, the forest around the shelter was lighted by a full moon on the snow pack, providing a glorious illumination for collecting both dead branches for fuel for the fireplace and soft branches for sleeping pads in the shelter. The moon and fire light was very much needed because our cold flashlights only glowed unless the batteries



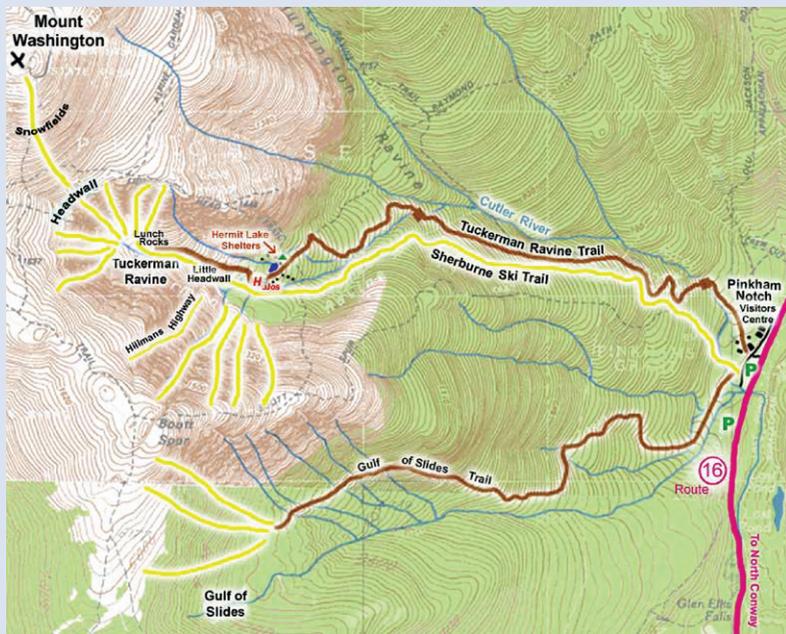


Figure 1.3 Trails leading to Mt. Washington, New Hampshire. From the Pinkham Notch Visitors Center to the Hermit Lake Shelter is 2.4 miles (3.9 km).

were warmed in our pockets or at the fireplace. It was not a quiet place. Besides the roar of the wind through the trees, there often were cracks like gun shots that we blamed on frost in the trees. We wondered if the temperature was not exceptionally low to produce such natural tympani.

Toward the interior back of the shelter, the dirt floor was mostly free of snow. To avoid the frozen ground, a thick stack of evergreen branches served as rough, fragrant bunks. Nevertheless, even using two sleeping bags, we were so chilled that by the middle of the night, we had to climb out of our sleeping bags and exercise to generate some body heat. Of course, the wind had long since blown out any embers in the fireplace. Frostbite in our feet was a concern even during daylight because my rubber boots were surely poor insulation.

At daylight, we were anxious to build a fire for heat and breakfast. While collecting more firewood, we found farther up the ravine a small, locked, emergency shed named "Howard Johnson" on our maps. It had a recording thermometer which revealed our night had just dropped to -29°F (-34°C) with a wind chill much colder. After breakfast, *Bob* and I donned our snowshoes and *Fred* clipped on his skis to climb Lion Head Ridge through very deep powder snow. There were enough trees on the lower parts of the steep ridge slopes to help us pull ourselves up the more difficult terrain. Above the crest of the ridge we reached a broad, smooth, upward-sloping,



Figure 1.4 From left, me, Bob (with ski poles), and Fred leaving Hermit Lake Shelter to climb northward along Lion Head Trail here at the upper left rear (January 31, 1948).



Figure 1.5a Bob on the wind-packed slope of Alpine Garden. See his shadow in a bright, sunny day (January 31, 1948).



Figure 1.5b Looking south down toward Tuckerman Ravine from the turnaround point on the summit cone. Note the long shadows of the sunny, but late afternoon on January 31, 1948.

wind-packed, icy terrain named “Alpine Garden” for its unique vegetation (Fig. 1.5a). By late afternoon, retreating back toward our camp became prudent. We glissaded down to the ridge beside the ravine (Fig. 1.5b, c). After the mountain gales, our shelter seemed homey.

After another frigid night, most remaining food was consumed in a recovering, leisurely breakfast and the trip out to Pinkham Notch was relatively easy. In contrast, arrival at the base lodge for warming before hitchhiking for home was not so pleasant. The wardens gave us hell for hiking into the Ravine without having



registered at the lodge, especially when the summit temperature had just fallen within two degrees of the record low of -50°F (-46°C). Also, he mentioned that the global record wind velocity for a half century, 231 mph (372 kph), had been measured on that summit. Due to respect for frequently stormy winds, the Summit Observatory is anchored by chains. Then he related accounts of several not-so-pleasant disasters under situations similar to our adventure with an added observation that we had been lucky, especially with snow-free weather.



Figure 1.5c Tuckerman Ravine on Mount Washington, New Hampshire. A more recent, mid-spring photo of Tuckerman Ravine showing the near vertical headwall used only by very expert skiers. Our route was up Lion Head, the buttress at the right edge of this view.

Another consequence of such Outing Club activities were the spontaneous growth of friendships, especially one with *Mary Westergaard*, a Swarthmore College graduate in chemistry and whose father was Harvard University's Dean of Engineering. She was employed also by the M.I.T. Biology Department, shared opinions on science and life, and would become my wife after I found a post-graduate income. A consequence throughout our lives was that we shared a chemical outlook on the universe, especially after her PhD in Physical Chemistry at Penn State in 1966. A special benefit has been her forthright editing of my writing.



Back at M.I.T., the universal requirement then for all undergraduates was a two year common sequence of courses in math, physics and chemistry, a particularly valuable background to imprint a quantitative bent crucial for later science. That attitude coloured courses in geological sciences, especially later on when learning about ore deposits. In his course on mineral deposits, *Prof. Patrick Hurley* presented the current theories of genetic processes for each ore type. He then dissected those ideas by elaborating on their defects. At that stage of development of understanding of ore genesis, the common attitude of economic geologists was that non-sedimentary ore deposits were generally products of magmatic activity. We students concluded that serious renovations were overdue in the conceptions of ore formation and that optimistically, maybe after graduation, our generation could further the science, a naïve but optimistic attitude.

The necessity for field experience was fulfilled by a required camp in northern Nova Scotia. Costs were a problem, especially for travel. Our class had few vehicles but had a unique and entertaining partial solution. *Sid Alderman* had brought a family car, a 1928 Rolls Royce to camp. It had a glass partition separating the front seat from a pair of folding jump seats and the large rear seat that carried many of us students. However, it was slow traveling because many of the roads, commonly unpaved red mud, were about 1.5 lanes wide, most of which was taken by that limousine. When we met a farmer coming from the opposite direction, he commonly slid into the universal deep roadside ditches trying to avoid a collision. Recognising that we had caused the problem, the very powerful, very low r.p.m. Rolls easily towed the grateful farmer back onto the road. Often he was sufficiently entertained by the situation that a casual friendship developed.

Opportunities to apply our training on mineral deposits were rare. Reality soon intervened. Finding employment was a challenge during the national recession in 1950, even with a degree from M.I.T. By touring the offices of mining companies in New York City, eventually the Peru Mining Company offered me a position if I would report to their office in Hanover, New Mexico. After hitchhiking across the country, I became their neophyte chief, and only resident geologist. However, fortune smiled there for two paramount reasons. *Harrison Schmitt*, a renowned authority on hydrothermal ore deposits, was both their exploration consultant and a superb coach for a newly minted geologist. In addition, the mining district was being mapped actively by the U.S. Geological Survey under the direction of *Robert Herton* (Kottlowski *et al.*, 1953). The friendly confrontations between these outstanding geologists on the nature of our “contact metamorphic” deposits and the adjacent Santa Rita porphyry copper deposit provided new perspectives for me and made clear that more than an undergraduate understanding was required. When Columbia’s *Prof. Charles Behre* toured our district with students that were studying aspects of supergene enrichment, he suggested that their graduate school could provide an improved comprehension of mineral deposits and their genesis. Graduate school became the obvious next stage in my life.



Again circumstances smiled with the enrollment of a remarkable class in Columbia's Department of Geology in 1952. Several of these new colleagues later made significant contributions to the development of geological sciences while at various institutions, including *Paul Barton* at the U.S. Geological Survey; *Wally Broecker*, *Paul Gast*, and *Taro Takahashi* at Columbia; *Bruno Gilletti* at Brown University; *William Kelly* at the University of Michigan and *Karl Turekian* at Yale University. Particularly stimulating for us during our graduate studies was ongoing vigorous research in several fields: in isotopic geochemistry with *Prof. Larry Kulp*, on the nature of ore deposits with *Prof. Charles Behre*, and on just-discovered continental drift with Columbia's Lamont Observatory Faculty. Our student-organised, early evening seminars concentrated on strategies by which one might deduce the origins of ore deposits. From those sessions grew an uncompromising faith that sufficient depth of understanding of genetic processes should stimulate practical applications for mineral exploration. That attitude at least partially justified my growing fascination with an intriguing quest for the origins of hydrothermal ore deposits.

1.2 Fascination with Ore Deposit Enigmas

Just after World War II, then current theories reasoned that igneous processes dominated the genesis of non-sedimentary mineral deposits. Not yet invented were quantitative approaches that would test such concepts and that eventually could support the construction of detailed models of the responsible processes. To start to create such models, it seemed reasonable to concentrate first on better resolving the physical conditions where hydrothermal ore deposits must have formed. Already in hand were several types of information that would guide us to better specify those conditions. At the time, environmental criteria could be derived from:

- (1) the thermal stability limits of ore and gangue minerals,
- (2) fluid inclusion compositions and filling temperatures in ore or gangue minerals,
- (3) distributions of various isotopic ratios and ages, and
- (4) comparisons with presumably analogous geothermal systems.

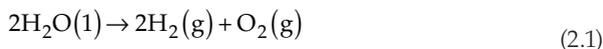
My dilemma was that after graduation, I wondered where could I further investigate mineral deposit theory while earning a living? To be effective in such research, I hoped for considerable freedom and extensive supporting facilities. The Geophysical Laboratory of the Carnegie Institution of Washington seemed then to provide an ideal environment for immersion in such entertainment and, in 1956, fortune provided a postdoctoral appointment helping me to follow my passion, understanding the genesis of ore deposits.



2.1 Redox Conditions

My initial objective at the Geophysical Lab in 1956 was how better to resolve the conditions where hydrothermal deposits must have formed. Progress on the physical environment was moving ahead following the various criteria mentioned above but, for the chemical environment, we were struggling. Aqueous and general physical chemists were focused very dominantly on temperatures between 25 and 60°C and rarely considered higher temperatures or pressures above 1 bar. A common and fruitful geochemical approach was to generate Eh-pH diagrams for each ore type as demonstrated by *Prof. Bob Garrels* (e.g., Garrels and Christ, 1965) and his graduate students at Harvard. Nevertheless, those diagrams were not so useful for many ore types because of poor resolution of both pH and Eh for higher temperatures and pressures. Spirited discussions of ore-forming redox environments ensued with *Paul Barton* of the U.S. Geological Survey who pointed out that if we disagreed that there was double the possibility that one of us might be correct. However, *Paul* and I soon concluded that there was a more direct redox parameter for aqueous environments, one that was clearly superior to Eh for conditions much above 100°C. We asked ourselves why we should not use either oxygen pressure or better, fugacity (Lewis, 1901) or its corresponding thermodynamic activity, a_i (Tunell, 1984). Interrelationships among these parameters can be appreciated readily by the following functions.

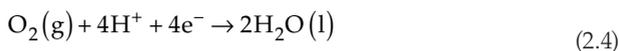
The redox state of a hydrothermal solution was obviously described at least at equilibrium by the reaction:



where at equilibrium:

$$K_T = \left(a_{\text{H}_2(g)}^2 \times a_{\text{O}_2(g)} \right) / a_{\text{H}_2\text{O}(l)}^2 \quad (2.2)$$

with half-cells in coexisting, equilibrated aqueous solutions of



which can be evaluated with the Nernst equation at a temperature, T, by

$$E_R = E^0 - \frac{RT}{nF} \ln \left[a_{\text{H}^+} / a_{\text{H}_2(g)}^{0.5} \right] \quad (2.5)$$



to which Eh is related by:

$$Eh = E_R \quad (2.6)$$

Consequently, Eh is a function of both a_{H^+} and a_{H_2} (or alternatively, a_{O_2}) giving it a dual dependence on the two parameters, acidity and redox state. In contrast, at equilibrium a_{O_2} (g) or a_{O_2} (aq) are independent variables indicating exactly the redox state and they are often directly measurable under many different conditions (Chou, 1987; Heubner, 1987). Diagrams intended to circumscribe the environmental conditions of hydrothermal deposition would be better designed by adopting the variable “log a_{O_2} ” as the ordinate rather than Eh. Isothermal stability boundaries at constant redox state on an Eh-pH diagram have an inclined slope set by the RT/nF factor of the Nernst equation but those on log a_{O_2} – pH figures are often orthogonal (for example, see Fig. 3.6). In 1961, *Gunnar Kullerud* and I published probably the first such diagrams for hydrothermal environments that used log P_{O_2} (Barnes and Kullerud, 1961). *Gunnar*, after action in the Norwegian Underground during World War II, devised methods for evaluating sulphide phase equilibria and became noted for his lab’s publications from the Carnegie Institution Geophysical Laboratory. Our applications, emanating from Fe-S phase relations, were to hydrothermal iron-containing systems and useful to 250°C. They included a treatment of acidity at elevated temperatures and with that addition they carried more conviction than earlier diagrams for several reasons. About two decades later, a neat comparison of the Eh – pH and Log a_{O_2} – pH diagrams was published by Henley *et al.* (1984). Remarkably, both of these diagrams continue to be used commonly by today’s geochemists.

2.2 Acidity

Similar to the Eh problems at high temperatures, there continued to be to an inadequate evaluation of the acidity function under such conditions. For redox-acidity diagrams to be applied to high temperatures, a problem was that the abscissa, pH, was poorly resolved due to a dearth of precise measurements. By 1960, there had been published only very rare determinations of acidity in aqueous solutions at high temperatures and pressures and these stemmed only from comparatively simple experimental lab systems. The application of those acidity measurements to ore solutions was at best problematical. As with the Eh discussion with *Paul Barton*, the resolution of the acidity problem came again from interaction with a visiting colleague. *James Ellis*, from the Department of Scientific and Industrial



Figure 2.1

Prof. Dr. Ulrich Franck, University of Karlsruhe, 2004.



Research of New Zealand, visited the Geophysical Laboratory and gave a seminar on his geothermal research progress. Afterward, he remarked on problems with resolving the acidity of hydrothermal solutions and explained that answers were forthcoming from studies underway at the Oak Ridge National Laboratory. There *Ulrich Franck* (Fig 2.1) explained that he had used aqueous electrical conductances to evaluate ionisation constants most crucially for water and also for solutions of HCl, KCl, and KOH, to about 800 °C at pressures extending above 2 kilobars. I wrote to *Dr. Franck* and his response to my letter and his reprints opened a life-long friendship. His initial results were all published in German (Franck, 1956a, b, and c) in a journal then not so often used by geochemists (*Zeitschrift Physicalische Chemie*) so remained underappreciated by Earth scientists. His work was soon reputed to be of Nobel Prize calibre and under consideration for that award (Nobel Symposium, 1981). Those were the key data necessary at the time for evaluating acidity in hydrothermal systems. They were the ionisation constants for water, and for solutions of the alkali chlorides and hydroxides. Without those, it was impossible to calculate the pH of the principal solutions of many hydrothermal systems. Only a few measurements of K_w that had been published by 1970 and

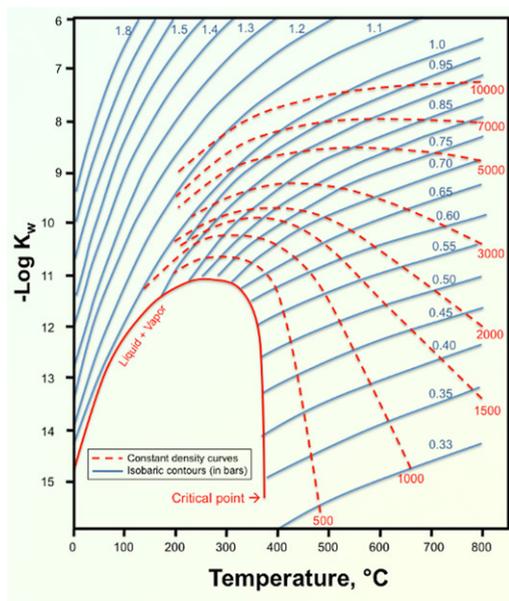


Figure 2.2

The ionisation constant of water (modified from Seward and Barnes, 1997; data from Marshall and Franck, 1981). The critical point is at 373.99 °K, 220.64 bars and a water density of 0.322 g/cc.

they deserved confirmation. Recognising that critical need, for his doctoral thesis *Jim Fisher* used conductance measurements in our lab to provide additional values along the liquid–vapour P-T curve to 350 °C (Fisher and Barnes, 1972). We were especially pleased with his results. For three years, he wrestled with problems of producing ultrapure water and with failure of 10 of our 12 expensive, custom-fabricated, sintered sapphire insulators. *Jim's* faith in our designs and endurance were remarkable before, eventually, an electrode performed. His persistence was rewarded with the needed data obtained finally in only two months. Since then, there have been many more such experimental measurements and the results are compiled in Figure 2.2.



The range in pH for specific pressures and temperatures can be determined from pertinent K_w 's from Figure 2.2 where:

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} \quad (2.7)$$

By assuming that the limits to the activities of a_{H^+} and a_{OH^-} are each roughly 10 (which bracket the range of pH), then the minimum pH is temperature – *independent* and is always:

$$\text{pH}_{\text{min}} = -\log a_{\text{H}^+_{\text{max}}} = -1 \quad (2.8)$$

and the maximum pH at $a_{\text{OH}^-} \sim 10$ varies with K_w :

$$\text{pH}_{\text{max}} = (-\log a_{\text{H}^+_{\text{min}}}) = (\log a_{\text{H}^+_{\text{min}}} - \log K_w) = (1 - \log K_w) \quad (2.9)$$

so that at 25°C, where $K_w = 10^{-14}$ then the maximum pH is about 15. Neutrality at all temperatures remains at:

$$\text{pH}_n = (-\frac{1}{2} \log K_w) \quad (3.0)$$

With my colleagues, we further examined the utility of these constants for thermodynamic implications initially with *Gary Ernst* of the Carnegie Institution Geophysical Laboratory (Barnes and Ernst, 1963) and a little later with *Hal Helgeson* and *Jim Ellis* we compiled and published the available ionisation constants needed for calculating the pH for hydrothermal conditions (Barnes *et al.*, 1966; Barnes and Ellis, 1967). These were the critical constants that everyone used at that time as the preferred parameters for constructing $\log a_{\text{O}_2}$ – pH diagrams to demarcate the environments that generated the common Fe-containing, hydrothermal deposits up to 250°C (Barnes and Kullerud, 1961).

2.3 Nature of the Fluids

We could analyse the behaviour of hydrothermal solutions in ore-forming processes only if we had reliable data for their volumetric and thermal states. In the 1950s and 60s, geochemists were appalled that physical chemists did not have available tables of both volumetric and thermodynamic properties of water and of halide and sulphate solutions to high temperatures and pressures. We needed that information for thermodynamic calculations ideally to about 1,000°C and 10 kilobars, most crucially for water and for saline solutions. Consequently, volumetric data for conditions up to geologically useful temperatures and pressures were starting to be developed. Early examples were by *George Kennedy* and geochemical colleagues at Harvard for H_2O (Kennedy, 1957) and $\text{NaCl-H}_2\text{O}$ (Sourirajan and Kennedy, 1962). Furthermore, the data for water were extended by *Wayne Burnham* (Fig. 2.3) and his students at Penn State (Burnham *et al.*, 1969) beyond the Steam Tables (Bain, 1964).





Figure 2.3 Wayne Burnham at the 1999 Goldschmidt Conference, Cambridge Massachusetts.

Although *Wayne* was a genius for reaction vessel design and operation, the experiments in his lab were commonly tests of the crews' endurance. The internally heated reaction vessels, when operated at the important upper levels of temperatures and pressures, were near their design limits and required for operation the devotion of a full time mechanic, a post-doctoral fellow, us his collaborators, and *Wayne*. Runs were assembled in an internally heated reaction vessel, which was then enclosed by a $\frac{1}{4}$ inch thick steel canopy that was mobile on roller skates, and finally heated to the intended run conditions. An experiment continued as long as possible commonly ending by equipment failure, usually due to burning out of the heaters or, more emphatically, by failure of pressure seals. The vessels were mounted vertically so that end seals and thermocouples, when ejected, would travel downward with no hazard, or upward, sometimes through the steel shield, and into the masonry

ceiling. Innocents in the overlying rooms had to be reassured that their floor was a safe shield from *Wayne's* experiments even though the boom was disconcerting. To obtain the most complete results, a run would continue as long as the system would remain intact, typically for several tens of hours during which tending was required.

The products of the volumetric measurements were thermodynamic P-V-T data, permitting calculations of hydrothermal solution behaviour: specific volumes, Gibbs free energies, enthalpies, entropies and fugacities. Since 1970, there have been published very many compilations of these parameters, including the additional, especially geochemically important components KCl, CaCl₂ and CO₂; see for examples Naumov *et al.* (1974) and the current Thermodynamics of Geothermal Fluids, edited by Stefánson *et al.* (2013). We can be proud of the predominance of geochemists over physical chemists among the laboratories that were generating reliable hydrothermal data. Our compulsion to develop a quantitative understanding of hydrothermal processes was the initiative to obtain data on how much and which metals could be transported in nature to produce valuable mineral concentrations.



The *physical conditions* accompanying ore deposition had already been roughly circumscribed by the 1960's. Depositional temperatures came primarily from three methods, by using: (1) fluid inclusion filling temperatures, many measured by Edwin Roedder (1967) of the U.S. Geological Survey and his successor, Robert Bodnar (1993, 2006) at Virginia Polytechnic Institute (2) various mineral stability geothermometers, and (3) approximations of temperatures based on geothermal gradients and overburden reconstruction. Still, the *chemical conditions* active at the local acidity and redox states during deposition were only vaguely prescribed for those environments. We did have measured thermodynamic stabilities of many ore minerals, which had been published for the temperatures of interest to over 500°C, which helped to explain their assemblages. However, there were *very few* data extant for the dominant aqueous complexes that controlled the solubilities of those minerals. That was the crucial gap. If one could find, estimate, or measure the stoichiometry and stability of such complexes at ore-forming pressures and temperatures, then solubilities could be contoured in terms of $\log a_{\text{O}_2}$ versus pH to conclude how hydrothermal transport had occurred. From that insight, we thought that we should be able to deduce what reactions must have caused precipitation and why at the observed locations. The causes of deposition would also be implicit from an exact determination of aqueous solubilities. With a confident perception of the causes of ore deposition, a dividend could well be immediate applications to genetic models to account for mineral transport and deposition. Such models should be of great value as guides for prospecting methods. The void in crucial data to me was a stimulating challenge.

In the 1950s, data on either solubilities or aqueous speciation were very rare for the components even of the common ore and gangue minerals. It was essential to obtain measurements of solubilities of ore minerals at pressures to about 1-2 kilobars and temperatures from 100°C to at least 600°C. If the solubilities were precise and extended over a sufficient range of solution compositions, then dependence on ligand concentrations would provide at least preliminary stoichiometric evaluation of the solubility-controlling complexes. Thus, it was clear that a totally new experimental programme had to be devised as no other labs apparently had an incentive to make such measurements, especially with H₂S being an important constituent of the sulphide-depositing fluids. H₂S is, of course, a hazardous material for which there were then inadequate data on aqueous solubility, P-V-T behaviour and ionisation constants (Schoonen and Barnes, 1988). The importance of hydrothermal solubility data stimulated my already thriving compulsion to design or adapt experimental facilities for such investigations and the Geophysical Lab protocol encouraged building or borrowing the necessary equipment.



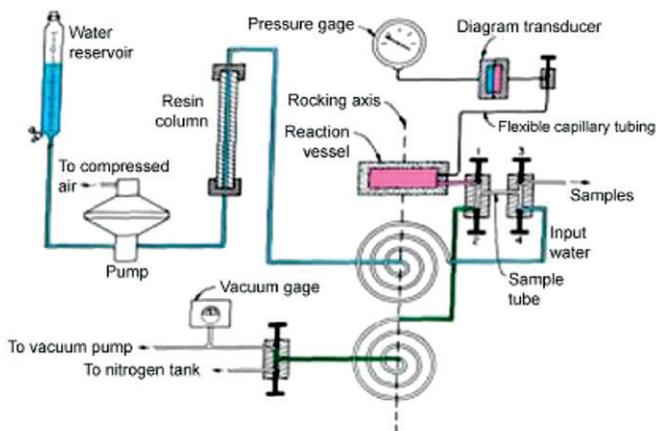


Figure 3.1 A schematic plan of the fixed volume system for sampling of hydrothermal fluids up to about 800°C and to about 0.5 kilobar. The reaction vessel rocked on a horizontal axis through a 30° arc at 36 rpm to optimise mixing and reaction rates (modified from Barnes, 1963).

A prime virtue of the Geophysical Lab was the daily gathering of the staff for lunch around a large, round, oak table where the enigmas of science were examined incisively and where difficult problems were considered to be intellectual games. Decades of the staff's experimental experience were soon focused on my proposed designs until a feasible synthesis emerged for high temperature and pressure measurements. The new design involved a dual-valve autoclave system that allowed us to carry out experiments through quantitative input as well as extraction of solid, liquid, and gas components. It was a closed system. Each run contained separately weighed solids, liquids and gases, permitting at high pressures and temperatures the extraction of small, <5 ml, fixed volume liquid or gas samples. I published that design, Figures 3.1 and 3.3 (Barnes, 1963) and updated it after extensive use (Barnes, 1971, 1981; Bourcier and Barnes, 1986). Another design that was used frequently in our lab and elsewhere depended on fluid flow at a known, pumped, rate (Seyfried *et al.*, 1979; Potter *et al.*, 1987). Compared to this flow system, the advantage of the closed system in Figures 3.1 and 3.3 was that the periodic extraction of samples made it easy to follow even very slow reaction rates. The flow-through systems could not provide that luxury as the volume of exchanged fluids eventually would become awkward.

Although we had a working autoclave system for high temperature and pressure experiments, the type of autoclave metal could be improved for better corrosion resistance and both static and creep strength (Ulmer and Barnes, 1987). We initially adopted common, easily machined 316 stainless steel (with 17 wt% Cr), which was used for very many experiments in the 1960s and 1970s, especially because of its tolerance of H₂S. However, a visit in 1983 to *Zhu Jinchu* (Fig. 3.2)



at the Nanjing Institute of Geology and Mineral Deposits started a reconsideration. In friendly chiding, he explained that their laboratory had found remarkable durability and performance with vessels made of Ti-17, an alloy dominantly of titanium containing 17 wt% of other metals for improved creep strength. Immediately we decided to test the new alloy, although it was not easily obtained in the U.S. Subsequently, *Zhu's* alloy became the standard for our autoclave alloy.

During construction of the first rocking autoclave system, the prime question was what would be the geochemically most informative mineral whose solubility should be measured with geochemically common ligands in hydrothermal fluids? The choice was influenced by my intimate exposure to the Hanover zinc-lead-copper deposit in New Mexico, U.S.A. during daily guiding of mining over two years. Sphalerite (or zincblende, $(Zn_xFe_{1-y})S$) immediately came to mind because of its relatively simple stoichiometry among ore minerals. Also sphalerite was especially common in several other types of hydrothermal ore deposits and geothermal systems (Krupp and Seward, 1987; Hayashi *et al.*, 1990). Having settled on an experimental system and a mineral for the first solubility investigations, the next step was to deduce which solvents should be evaluated that would be geochemically reasonable.



Figure 3.2 Zhu Jinchu, Nanjing Institute of Geology and Mineral Deposits.

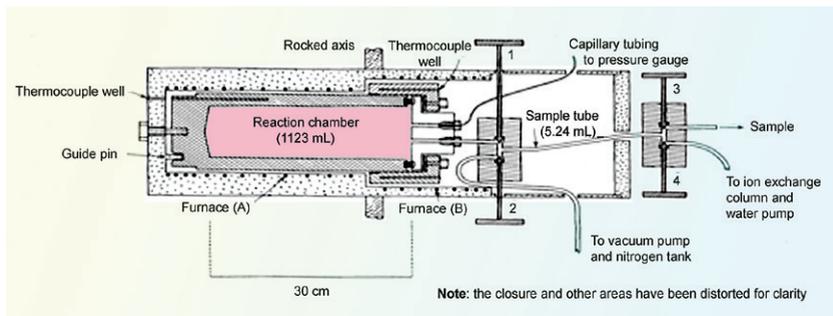


Figure 3.3 Configuration of an hydrothermal reaction vessel fitted with valves for sampling from elevated conditions (modified from Barnes, 1963). A similar but later, higher pressure-temperature model is illustrated in Ulmer and Barnes (1987, Fig. 8.1).

3.1 The Urgency to Understand Metal Complexes in Solution: Hard and Soft Choices

To deduce which aqueous species in hydrothermal fluids must have carried the metals into an ore deposit and at what concentrations, we needed to evaluate both the thermodynamic stabilities of each potential complex and the ligand concentrations of the transporting solutions. At that time, the practical means of determining thermodynamic stabilities of aqueous metal species at elevated conditions was by solubility measurements. That depended upon sufficiently accurate solubility measurements over a broad range of ligand concentration (Barnes, 1981). However, *which metal complexes might have been involved?* Soon, a means was devised for estimating solubility behaviour that should be expected for metals in aqueous solutions. A guide by Pearson (1963) appeared on the expected stability of many solubility-controlling aqueous complexes. This compilation provided perspective on potential complexing and transporting agents for ore minerals and it was testable against new solubility data for sphalerite. Pearson's "Hard – Soft, Acid – Base Principle" correlated the strength of complexing among metals and ligands (Pearson, 1963; for its historical development, see Rickard and Luther, 2006, and Stumm and Morgan, 1981, Chapter 6, and for its applications to hydrothermal systems, see Seward and Barnes, 1997).

Pearson's acid-base classification (see Table 3.1) generalised that the harder metals preferred complexing by harder ligands, both being more ionic, in contrast to the more polarisable and covalent softer metals and ligands. Zinc was intermediate, potentially being complexed by either the hydrothermally abundant, harder chloride or hydroxide or maybe the softer bisulphide ligand. An interesting possibility was to explore, at the proper redox and acidity conditions, if there were significant complexes with the dominant sulphur-containing anion, HS^- in equilibrium with ZnS , in spite of predictions otherwise. Other soft ligands considered included thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and polysulphides (S_x^{2-}).

Table 3.1

Classes of metal complexation behaviour (after Pearson, 1963, 1997; Leach, 2013).

Hard	Intermediate	Soft
Al^{3+} , Fe^{3+} , Co^{3+} , Sn^{2+} , Sn^{4+}	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}	Cu^+ , Ag^+ , Pt^{2+} , Au^+ , Hg^+ , Hg^{2+}

In contrast to inorganic species, only much later in this era were organic compounds also investigated (Landais and Gize, 1997; Seward and Barnes, 1997; Shock *et al.*, 2013). Nevertheless, Pearson's correlations suggested that the soft metals would be more readily complexed by HS^- or $\text{S}_2\text{O}_3^{2-}$. Following this soft-soft correlation, we set out to determine the geochemically necessary equilibrium constants for several metals by measurements of hydrothermal solubilities (Pearson's early scheme, although very useful in the early 1960s, is not trouble-free and should be considered with caution as explained by Leach, 2013).



Consequently, hydrothermal solubilities were measured for the common metals of hydrothermal ores initially at the Geophysical Laboratory of the Carnegie Institution and, after 1960, in an expanded lab at Penn State University. In four years at the Geophysical lab (1956-1960), most measurements were intended to determine the strength of bisulphide complexing although ill-advised detours into solubilities in aqueous polysulphide solutions also were explored. In the absence of any published data on the solubility of metal sulphides in water-immiscible hydrogen polysulphide liquids, I synthesised some first to check for density, colour and refractive index. The second stage, to make solubility measurements in that fluid, was never achieved. At home after a day of polysulphide fluid testing, a phone call announced that my hood had its glass windows blown out and there was considerable damage to much of the lab. About 300 ml of polysulphide liquid had exploded distributing yellow-green pasty blotches on the walls and left a horrendous stench that was never entirely removed. So, afterwards the lab door was left closed and the windows were open on purpose.

My plan was to experimentally evaluate the complexation constants of the ore metals by working with graduate students and postdocs, ideally astute chemists with polished lab skills and and comprehension of ore geology. The odyssey began with the Pearson intermediate-class metal, Zn, and measured solubilities primarily of sphalerite to investigate the transporting potential of chloride versus bisulphide complexing (Barnes, 1963). Later together with *Bill Bourcier*, we improved the data set for Zn complexes (Bourcier and Barnes, 1987). Solubility measurements from our Penn State lab also included ore minerals of copper (Crerar and Barnes, 1976), lead (Giordano and Barnes, 1979), silver (Gammons and Barnes, 1989), gold (Shenberger and Barnes, 1989), and mercury (Barnes *et al.*, 1967; Barnes and Seward, 1997). At the time, such measurements were not carried out in many labs around the world and the Penn State lab was one of ten which early on produced experimental data on the aqueous complexing

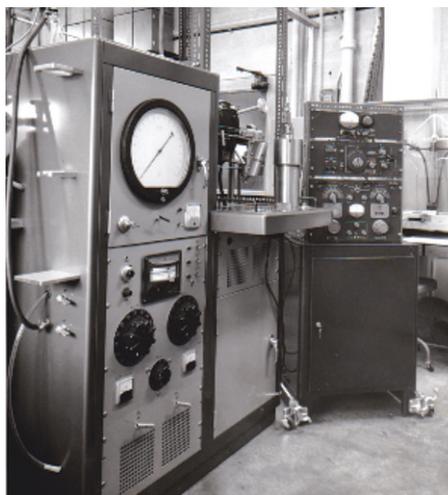


Figure 3.4 Our hydrothermal system at Penn State at about 1964, a custom model manufactured by Scientific Systems, Inc., Bellefonte, Pennsylvania. A 1.1 litre reaction vessel (bomb) is on the shelf in the upper centre with a conductance bridge on the right rack and the pressure-temperature controlling and measuring systems in the left cabinet.

of at least two hydrothermal ore elements. Those labs, listed in Table 3.2, were located mostly in the United States with others in Canada, Switzerland, Russia, and the United Kingdom.

Table 3.2

Sources of experimental data from laboratories that published on aqueous complexing of multiple ore elements in hydrothermal solutions during the last half of the twentieth century, in alphabetical order.

Institution	Principal Scientists
Eidgenössische Technische Hochschule, Zurich	T.M. Seward
McGill University, Montreal	A.A. Migdisov; A E. William-Jones
Oak Ridge National Laboratory, Tennessee	D.A. Palmer; D.J. Wesolowski;
Pennsylvania State University	H.L. Barnes; C.W. Burnham
University of California, Riverside	F.W. Dickson; G. Tunell
University of Idaho	S. Wood
University of Maryland	G.A. Helz; G.W. Luther; J.A. Tossell
University of Minnesota	W.E. Seyfried
University of Toronto	G.M. Anderson; S.D. Scott
University of Wales, Cardiff	D. Rickard
Vernadsky Institute, Moscow	B.N. Rhyzenko; S. Malinin
Russian Academy of Science IGEM, Moscow	A.I. Zotov
Russian Academy of Sciences, Chernogolovka	K. Shmulovich

From these laboratories, many solubility data have ensued over the last 5 decades of the twentieth century. In Table 3.3, I have compiled the stoichiometries of some dominant complexes that have been resolved with more certainty since their initial evaluations in the 1960s. These complexes are dominant at typical pHs near 2 pH units below to 1 above neutral, at temperatures of 100-600°C, and at chloride and sulphide concentrations representative of natural hydrothermal solutions (Polster and Barnes, 1994; Yardley, 2005). Their associated equilibrium constants have not been included in Table 3.3, not so much due to potential changes in speciation but more because improvements in the resolution of those constants are still continuing.





Figure 3.5 Terry Seward.

Note that many of the above complexation data of Table 3.3 were products of *Terry Seward's* labs successively in Auckland, New Zealand at the Department of Scientific and Industrial Research, then in Zürich, Switzerland at the Eidgenössische Technische Hochschule and now at Victoria University in Wellington, New Zealand. As a migrant from home in Newfoundland, Canada, *Terry* has had a remarkable influence on hydrothermal geochemistry including as my coauthor. We have interacted on several continents, such as when I was presenting a short course in Sydney, Australia. *Di* and *Terry* invited *Mary* and me to weekend at their home in Wellington, New Zealand nominally to consider aspects of a joint publica-

tion. On arrival, we had a currency problem. Not having any New Zealand dollars, gracious host *Terry* paid our airport tax to export us back to Australia. What a collaborator!

Just at the end of the 20th century and after 5 decades of producing hydrothermal solubility data, a means was found for verifying the behaviour in nature of mineralising solutions with solubilities calculated from well-known complexation constants (Barnes and Rose, 1998). Thus further testing could be carried out by analysing the contents of single fluid inclusions at each paragenetic stage of ore deposition. The contents of an inclusion could be recovered by laser ablation for analysis by inductively coupled plasma mass spectrometry (LA-ICP-MS) as developed at the Eidgenössische Technische Hochschule (ETH), Zürich (Audétat *et al.*, 1998). The saturation state of each mineral at the stage of beginning of precipitation could be compared with the calculated solubility at the precipitation temperature. The ETH group found that in an eastern Australia tin deposit, the Yankee Lode, cassiterite deposition began when the measured concentration reached the calculated tin saturation level, a pleasing agreement. The calculated saturation concentration matched the observed, measured concentration at the paragenetic stage where precipitation of cassiterite first began. Similar results with other ore minerals gave reassurance that our chemical modelling was reasonably accurate for understanding the conditions for ore deposition.

The extent of that thermodynamic base has continued to expand for more ore elements, to a widening range of pressures and temperatures, for better specification and for constantly improving accuracies. The summary in Table 3.3 implies that the principal complexes of the ore metals are bonded to either chloride or sulphide ligands (Yardley *et al.*, 2011). Because both are important, this new set of data resolves the decades-long dissension of whether bisulphide complexes



contributed significantly to ore transport. For example for zinc, Tagirov and Seward (2010) have found that hydrothermal complexing by chloride is apparently dominant over that by the bisulphide ligand except where the salinity of the transporting solution was unusually low. Compilations of newer complexation constants for many metals can be found in Rickard and Luther (2006) and Sherman (2011).

Table 3.3 Aqueous complexes of interest for hydrothermal transport of metals. These complexes are considered to be predominant in aqueous liquids over other aqueous species, carrying the metals at particular, natural, relatively common combinations of conditions of pH, oxidation state, ligand concentrations and temperature.

Metal	Complexes					References
Ag		AgCl_2^-	AgCl_3^{2-}	AgHS^0	$\text{Ag}(\text{HS})_2^-$	1
Au		AuCl_2^-		AuHS^0	$\text{Au}(\text{HS})_2^{\pm}$	2
Co		CoCl_2^0	CoCl_4^{2-}	CoHS^+		3
Cu^+			CuCl_2^-	$\text{Cu}(\text{HS})_2^-$		4
Cu^{2+}		CuCl^+	CuCl_2^0	$\text{Cu}(\text{HS})_3^-$		
Fe		FeCl^+	FeCl_2^0	FeHS^+		5
Hg		HgCl_2^0	$\text{Hg}(\text{HS})_2^0$	HgHS_2^-	HgS_2^{2-}	6
Ni		NiCl^+	NiCl_2^0	NiHS^+		7
Pb		PbCl^+	PbCl_2^0	$\text{Pb}(\text{HS})_3^-$		8
Sn	SnCl^+	SnCl_2^0	SnCl_3^-			9
Zn	ZnCl^+	ZnCl_2^0	ZnCl_4^{2-}	$\text{Zn}(\text{HS})_2^0$	$\text{Zn}(\text{HS})_3^-$	10

1. Stefánson and Seward (2004); Pokrovski *et al.* (2013)
2. Zotov *et al.* (1990); Tagirov and Zotov (1996); Vicente *et al.* (1998); Akinfiyev and Zotov (2001); Stefánson and Seward (2004); Tagirov *et al.* (2006)
3. Migdisov *et al.* (2011)
4. Etschmann *et al.* (2010); Sherman (2011)
5. Heinrich and Seward (1990); Rickard and Luther (2006)
6. Barnes and Seward (1997); Rickard and Luther (2006)
7. Rickard and Luther (2006)
8. Giordano and Barnes (1979); Uhler and Helz (1984); Seward and Barnes (1997)
9. Sherman (2011)
10. Bourcier and Barnes (1987); Tagirov and Seward (2010); Mei *et al.* (2013)

Especially in the last few decades, there have been major improvements in powerful theories that can identify the structures and relative stabilities of aqueous complexes through modelling. The Pearson correlations have been supplanted by these much more powerful means of evaluating the stoichiometries and stabilities of hydrothermal complexes. In particular, the ability of very fast computers with



huge memory capacity to calculate accurate quantum mechanical energies and wavefunctions for large atomic clusters (generally termed “*ab initio*” modelling) began to have an important effect on geosciences in the 1980s (Lasaga, 1998).

Gerry Gibbs of the Virginia Polytechnic Institute pioneered their use in mineralogy. In the 1990s, *Tony Lasaga* of Yale University and coworkers introduced the application of *ab initio* calculations to the study of mineral-water interactions, atmospheric chemistry and geochemistry (see references in Lasaga, 1998). These *ab initio* results and statistical mechanical calculations predict stabilities with useful accuracy (Rickard and Luther, 2006; Lemke and Seward, 2008; Sherman, 2011). Calculated stabilities have been made by faster computers so that the results can now supplant those based directly on solubility measurements, especially where the modelling is confirmed by spectral data.

Advances in spectroscopy are also changing our comprehension of solution characteristics in hydrothermal chemistry. Two changes are especially important. From Raman spectra (Pokrovski and Dubrovinsky, 2011) and from *ab initio* modelling calculations (Manning, 2011; Tossel, 2012), there is agreement that the free radical, S_3^- , at above about 250°C becomes dominant over speciation long assumed to be SO_4^{2-} and H_2S or HS^- .

That means the common diagrams for sulphur species distribution with coordinates of $\log a_{O_2}$ – pH need to be revised again as suggested by Pokrovski and Dubrovinsky (2011) and shown here in Figure 3.6. That change in speciation may correct for calculated Au solubilities involving the older complexes that are well below those observed by fluid inclusion analyses (Kouzmanov and Pokrovski, 2012). The same is underway with newer Cu^+ speciation in chloride – sulphide solutions that also has been demonstrated by Mei *et al.* (2013).

A second discovery of major importance using the new molecular dynamics

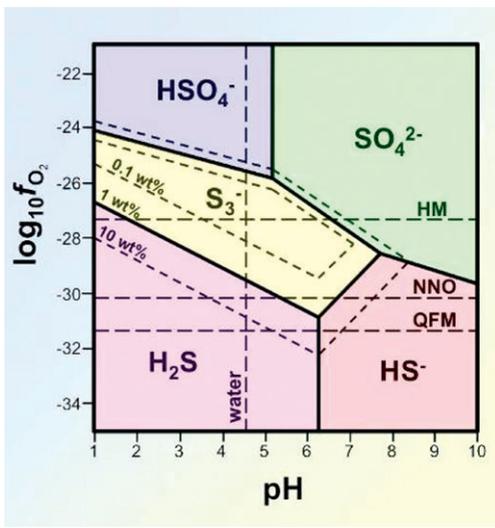


Figure 3.6

The stability field of dominant sulphur-containing aqueous species at $\Sigma S = 0.1$ -10 wt%, including especially the S_3^- radical at 350°C, and 0.5 GPa. The neutral pH is labelled “water” on the vertical dashed line. Dashed horizontal lines indicate the redox states for HM – haematite + magnetite, NNO – nickel + nickel oxide, and QFM for quartz + fayalite + magnetite (modified from Pokrovski and Dubrovinsky, 2011, Fig. 3).



tools is that hydrated free aqueous ions and molecules bond into clusters whose dominance affects the kinetics of dissolution and crystallisation (Casey and Swaddle, 2003; Rickard and Luther, 2006; Lemke and Seward, 2008). Clustering must speed both types of these reactions. Further challenges that molecular modelling should meet are to identify further the speciation of sulphur species to higher temperatures and pressures and the metal complexes associated with them, including with the S_3 radical.

3.2 Vapour Transport – Another Horizon for the Future

In the above discussions, I emphasised mostly progress made over the last decades on aqueous solubilities. The alternative of gas transport was not considered because vapour pressures of ore minerals up to a few hundred degrees were well known to be very low. So during the 1960s and even later, little credence was given to the possibility of significant vapour transport of the metals into hydrothermal deposits. The single recognised exception was for mercury vapour. In retrospect, we might as well have undertaken experimental investigations to test the hypothesis that other metals might also be vapour-transported. At that time, our myopic focus was tightly on ore element mobilities in inorganic complexes in aqueous liquids, but to the neglect of both organic and vapour species. Basically, we were busy with our aqueous investigations and neglected vapour transport. Since then, evidence has accumulated early in the 21st century that solubilities in gases are sufficient for important vapour transport not only in mercury deposits but also for epithermal and porphyry copper ores to carry Ag, Au, As, Cu and Mo (see the compilation in Kouzmanov and Pokrovski, 2012). Noteworthy are recent investigations that favour vapour transport by high vapour solubilities measured in the *Tony Williams-Jones* laboratory (e.g., Migdisov and Williams-Jones, 2013; Hurtig and Williams-Jones, 2014a,b; Migdisov *et al.*, 2014).

Recent analyses of vapour inclusions in quartz (Mavrogenes *et al.*, 2002; Seo and Heinrich, 2013) reveal that both copper and gold had been carried by low density hydrothermal fluids. Experiments with magnetite proved that $FeCl_2$ is gas-soluble enough to be vapour-transported (Simon *et al.*, 2004), similarly with copper sulphides by $Cu(HS)_2^-$ (Etschmann *et al.*, 2010) and also with ^{65}Cu fractionation to be vapour- carried (Rempel *et al.*, 2012). Active ligands included in ore-forming vapours are found by *ab initio* calculations to be H_3O^+ , NH_4^+ , and H_3S^+ (Lemke and Seward, 2008). Altogether, the vapour phase now must be viewed as a fluid capable of hydrothermally transporting important quantities of ore components (Heinrich *et al.*, 1999).

The P-T conditions where vapour transport could occur have been identified as shown in Figure 3.7. The three conditions of interest here are labelled as “Supercritical Fluid” or “Hydrothermal-magmatic vapours” or “Volcanic vapours”. Because the densities of the first two fluids are tenths of grams per cubic centimetre, they could be potentially effective solvents of ore components. The very low densities of volcanic vapours, some hundredths of grams per cubic



centimetre or less, make it certain that they will be less able solvents but they may act as physical carriers of volatile ore components. Apparent evidence of such transport is seen commonly around volcanic vents, fumaroles, with often vividly coloured coatings of surrounding rocks, *i.e.* sublimates. In addition to the expected sulphur and arsenic minerals, Pokrovski *et al.* (2013) report in their compilation appreciable concentrations of Cu, Sn, Mo, Pb, and W in sublimates. However, they conclude that there remain major challenges, both experimental and in modelling, to fully understand vapour transport of ore components, a status comparable to that of liquid solution transport decades ago.

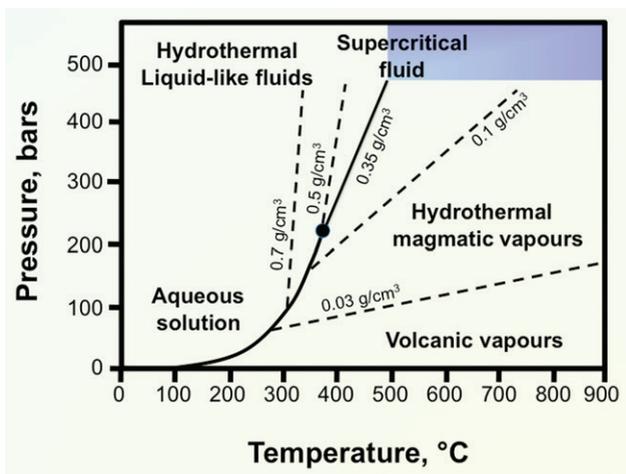


Figure 3.7

Regimes for various hydrothermal fluids compared to the densities and critical curve for water, the heavy line up to the critical point of water at 344.7°C, 215.4 bars (modified from Pokrovski *et al.*, 2013).



4. DEDUCING THE CONDITIONS WHERE ORES FORM

Innovative studies in the 1950s and 1960s that were defining the environments where ores had been deposited, especially those investigating the phase relations and thermodynamic stabilities of ore minerals, were concentrated in two world centres. Both were in Washington, D.C., at the U.S. Geological Survey with research led by *Paul Barton* and *Pete Toulmin* and at the Geophysical Laboratory of the Carnegie Institution of Washington with research led by *Gunnar Kullerud*. Their results were often introduced at the evocative, monthly meetings of the Geological Society of Washington and at the daunting, hypercritical sessions of the Geophysical Lab's Petrologists' Club. Early progress reports and summaries from the Geophysical Lab were reported in the widely distributed Carnegie Institution's *Annual Reports* often long before normal journal publications.

Besides the common use of filling temperatures of fluid inclusions to document ore deposition temperatures, additional hydrothermal geothermometers were being developed during those early years. There were two special geothermometers that were of general utility because of the common occurrences of quartz and of sphalerite in hydrothermal deposits. Their development will be followed here because they provided such extensive information for many types of ores, especially for the temperatures of hydrothermal deposition.

4.1 How the Geochemistry of Quartz Developed into the Most Valuable Geothermometer

Even casual observation of hydrothermal deposits reveals an abundance of quartz veins and coatings. This prevalence implies that any intrinsic depositional data that could be derived from this mineral should be especially valuable for genetic implications. Following that thought, by 1956 a study of the silica content of sampled geothermal solutions revealed that there was a strong correlation of silica concentration with fluid temperatures. Three geochemists from the U.S. Geological Survey, *Don White*, *W.W. Brannock* and *K.J. Murata* (1956) had discovered the quartz geothermometer. Since then, over 200 papers have been published on silica mineral geothermometry and related solubilities, several from *Bob Fournier's* research (e.g., Fournier and Potter, 1982). This geothermometer has evolved to become a routine tactic in the evaluation of geothermal fields. However, there are multiple factors that influence the concentrations of dissolved silica and make the temperature correlation with silica concentration complicated. For subcritical aqueous solutions along the liquid–vapour curve, there have been many measurements of the equilibrium quartz solubility that provide a reference calibration



curve to read an ideal temperature given a measured silica content of an aqueous sample. Nevertheless, non-equilibrium conditions can cause field concentrations to be either lower or higher than the ideal concentrations. The differences can be ascribed to the kinetics of dissolution and of precipitation, which were beginning to be understood.

The study of kinetics in geochemistry began in the 1960s and 1970s (*e.g.*, see Berner, 1978; Lasaga, 1981, 1998). Particularly appropriate kinetic data for hydrothermal solutions were the rates for quartz reactions with water but these were not measured until the late 1970s, initially by *Don Rimstidt* in our Penn State labs (Rimstidt and Barnes, 1980). Our objective was to use the measurements to model the rates of dissolution and precipitation by considering changes in silica concentrations due to the effects of nature's heating, cooling, mixing, or boiling. However, precautions were necessary to be certain that the applied rate measurements were absolute and not influenced by vagaries in the experimental conditions. Ideally, the measurements must be made with quartz particles with the lowest surface energy (equilibrium) so we modified the usual methods to minimise the extra surface energy arising from crushing of the material to prepare for our experiments. The more reactive, higher energy surfaces are more soluble and were removed preferentially by dissolution by washing with HF or NaOH solutions at ambient temperatures. Alternatively, quartz samples were heated in pure water to roughly 225°C for long enough for the silica concentration to become stabilised. Then the solution was quickly vented to prevent any precipitation during subsequent cooling. These three processes gave ideal starting materials with equilibrated quartz surfaces for later dissolution experiments. Since then, there have been many theoretical and experimental studies of the solubility and reaction rates of quartz and of the effects of acidity and alkali concentrations on these rates (Dove, 1994; Rimstidt, 1997; Lasaga, 1998).

The rates for quartz prescribe the range of temperatures over which equilibration could be expected and where this thermometer could be useful. Because the silica concentration in equilibrium with quartz increases with temperature, a silica concentration identifies its equilibrium temperature. Below about 100°C, the rate of quartz dissolution is slow enough that undersaturation could be expected in nature at such temperatures but instead, below about 150°C, supersaturation is more common due to the control of silica concentration by the solubility of precipitated silica-containing minerals with faster reaction kinetics than quartz. Therefore, the quartz geothermometer has its best accuracy above about 150°C. Above about 300°C, and to the critical point at 374°C, the solubility is high (Hunt and Manning, 2012) and the rate of dissolution is fast but at such high solubility, boiling or cooling can quickly cause supersaturation above quartz solubility. For example, at Wairakei, New Zealand, the apparent hydrothermal temperature by the quartz geothermometer is 10 – 20°C too high, even for actual temperatures of 220 – 230°C (Lovelock, 1995). The continuing development of the quartz geothermometer now has led to regression equations for the reference curves that depend upon the experimental enthalpy as a function of temperature and measurements



of silica concentrations. These equations have been tested, for example, with data from the Los Azufres geothermal field that revealed an accuracy of $\pm 18^\circ\text{C}$ at $240 - 300^\circ\text{C}$ (Verma, 2012).

The ideal silica solubility curve is based on equilibration with quartz as a stable solid with no excess energy contributions from textural or structural states or disequilibrium processes. Geothermal systems often have other silica phases contributing to their hydrothermal concentrations, such as the silica glass or cristobalite of volcanics, or previously precipitated amorphous silica or chalcedony (mix of quartz plus moganite), each of which have higher solubilities than quartz. Consequently, these other silica phases may dissolve to raise the silica concentration above that of quartz causing an anomalously high apparent crystallisation temperature. In fact, comparison of quartz-based temperatures with directly measured geothermal temperatures below about 150°C have, not uncommonly, shown such apparently inaccurate temperatures. Corrections can be made for equilibrium with specific silica minerals by using reference solubility – temperature equations that are available for both chalcedony and amorphous silica (Karingithi, 2000). Also, there are some rate data from our lab for dissolution and precipitation of cristobalite over the useful range of $150 - 300^\circ\text{C}$ (Renders *et al.*, 1995). These rate data can be used for modelling of cristobalite geothermometry just as has been done for quartz.

Don Rimstidt and I modelled the representative behaviour of the quartz geothermometer along the P-T, liquid – vapour curve of water as shown in Figure 4.1 (Rimstidt and Barnes, 1980). We selected fluid ascension rates to be along typical gradients like those of the 3×10^{-5} m/sec at El Tatio, Chile. The ratio of A/M (reactive area in m^2/mass of solution in kg) that is assumed at $100 \text{ m}^2/\text{kg}$ is equivalent to the textures of a very fine grained sediment; comparatively a vein 0.1 mm wide would have an A/M of $20 \text{ m}^2/\text{kg}$.

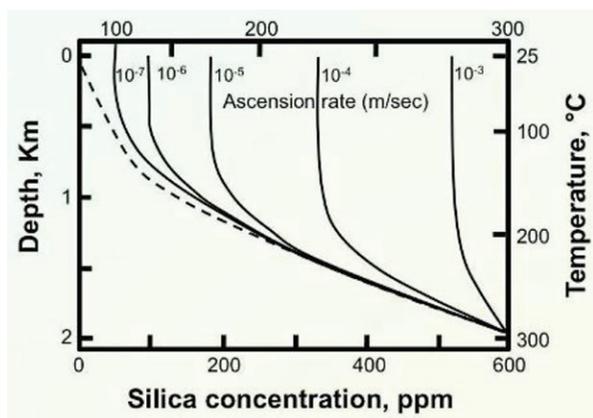


Figure 4.1 The effect of the ascent rate on the quartz geothermometer temperature. Assumed are a geothermal gradient of $138^\circ\text{C}/\text{km}$ and an A/M of $100 \text{ m}^2/\text{kg}$ (modified from Rimstidt and Barnes, 1980).



The results of these silica investigations were to provide a particularly useful geothermometer applicable to hydrothermal environments wherever fluid samples could be found and analysed for silica content. The method has been especially useful for geothermal systems to determine the temperature of the reservoir source of fluid samples. There is a complementary method for sulphide ore deposits. Again, the widespread occurrence of sphalerite makes it a special geothermometer to determine the palaeothermometry of its crystallisation.

4.2 The Nature of Sphalerite Geothermometry and Geobarometry

Even superficial observations reveal that the sphalerite of lower temperature hydrothermal deposits, such as in Mississippi Valley-type deposits, is generally light coloured with cream to light brown tints. In contrast the sphalerite of higher temperature deposits, such as those deposited near intrusive contacts, is typically amber-brown to nearly black. This variation suggests that in these Zn-Fe-S solid-solutions, the solid solution composition controls the colour and might be sufficiently temperature-dependent to be useful as a geothermometer. *Gunnar Kullerud* attributed the colour to the FeS content of sphalerite and reported the composition as a geothermometer (Kullerud, 1953). However, by examining the reactions that produce the sphalerite solid solution, it is apparent that other variables besides temperature must affect the FeS-content, even where in equilibrium with coexisting pyrrhotite (Fe_{1-x}S where $x = 0-0.2$). Possible reaction paths among the dominant aqueous species that could form sphalerite are:



The equilibrium of most interest to the sphalerite solid solution is:



The extent of solid solution in *equilibrium* with pyrrhotite can be attributed to five parameters. These are (1) the FeS content of pyrrhotite, (2) the activity of S_2 gas, (3) the concentrations of other elements in solid solution, plus (4) temperature, and (5) pressure. The FeS activity is simply dependent on temperature and pyrrhotite composition, which directly correlate with a_{S_2} .

Decades of research since *Kullerud's* pioneering investigation have provided sufficient data to judge the relative importance of each of these parameters and some of these will be discussed below.

Among the pertinent parameters listed above, the effects of trace elements on the FeS-sphalerite solid solution could be to alter the solubility of FeS in sphalerite. Very many analyses have shown that only 9 other elements are common in sphalerite: As, Cd, Co, Ga, Ge, In, Mn, Sn, and Tl (*e.g.*, Cook *et al.*, 2009 and included references), with most at very minor concentrations except for Cd and Mn (Wright, 2009). However, at normal concentrations, these latter two elements apparently have little effect on the FeS content of sphalerite (Balabin and Urusov,



1995). Therefore, normally we can neglect the effects of the other elements and may interpret the pyrrhotite-sphalerite solid solution as if it were within the ternary, Zn-Fe-S system only.

The effect of pressure on the FeS content of sphalerite at a fixed temperature and pyrrhotite composition was examined initially by Barton and Toulmin (1966), who made an approximation of its magnitude. Their experiments on sphalerite compositions were carried out mostly in the lab of *Gunnar Kullerud*, and in collaboration with him, with the intention of resolving an earlier conflict over temperature versus pressure effects on sphalerite compositions. The fact is that the pressure effect depends upon the molar volume change of the FeS component between pyrrhotite and sphalerite, a value that is not negligible as has been more precisely determined by Martin and Soler I Gil (2005). Therefore, the FeS content of sphalerite in equilibrium with pyrrhotite must be pressure-dependent as well as temperature-dependent. This is nicely illustrated by a divariant surface shown by Figure 4.2, where the surface is bound by edges at the Fe + FeS and at the pyrite + pyrrhotite univariant curves (Scott and Barnes, 1972). In our work at the time to determine the divariant surface, *Steve Scott* and I followed the recipe given in the conclusion of the paper by *Paul Barton* and *Pete Toulmin* (Barton and

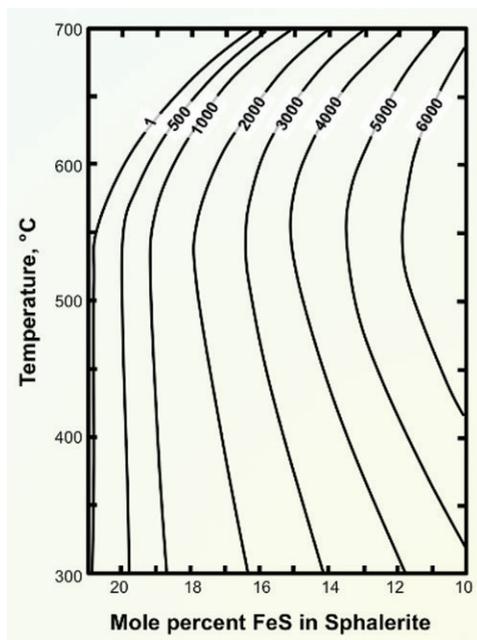


Figure 4.2 Sphalerite composition in equilibrium with hexagonal pyrrhotite contoured at pressures from 1-6,000 bars (modified from Scott and Barnes, 1972).

Toulmin, 1966) to better calibrate sphalerite compositions versus temperature and pressure. This was done specifically as a basis for modelling their use for geobarometry. Note that the thermodynamic parameter, $S_2(g)$, is useful to correlate the temperature and pressure-dependence of the FeS content of both sphalerite and pyrrhotite. Later investigation of the uncertainties in such applications were reported by Martin and Soler I Gil (2005) who illustrated this by their Figure 6, included here as Figure 4.3. They also give examples of applications to 14 sites with pressures up to 8,500 bars. The variety of their applications exemplifies the utility of this indicator because of the geologically frequent occurrence of sphalerite together with hexagonal pyrrhotite (Scott, 1976).



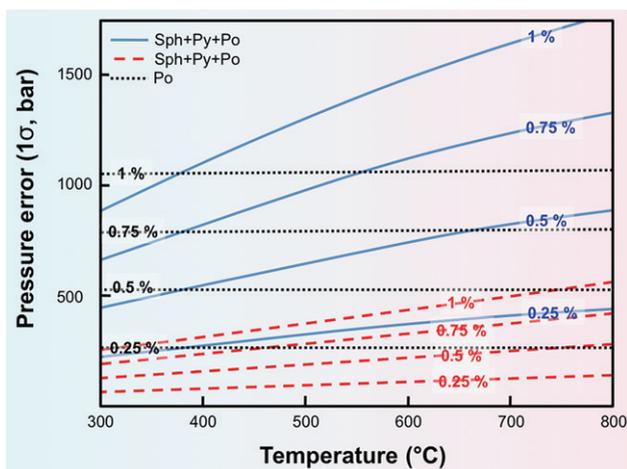


Figure 4.3 Temperature-dependence of the uncertainty in pressure deduced from the FeS content of sphalerite in equilibrium with assemblages among pyrite, pyrrhotite, and troilite (modified from Martin and Soler I Gil, 2005).

4.3 Evidence of Environmental Conditions from Ubiquitous Iron Sulphides

Common even in ancient reports on hydrothermal deposits were detailed observations of the characteristics of each ore's iron sulphides. The specific minerals found and their particular forms and textures were documented. The persistence and variety of particular characteristics, in portions of single deposits, and also among groups of deposits, implied that their crystallisation must be controlled by processes that were consistently reproducible in hydrothermal environments. Why a wide variety of types of iron sulphides should occur was largely hypothetical until studies began to supply thermodynamic and kinetic data on their crystallisation reactions. Discussed below will be these minerals, their forms and morphologies and their implications for the conditions under which these sulphides must have been deposited.

Intuitively, the differences in binary compositions among the iron sulphides pyrite, marcasite, greigite, smythite, pyrrhotites, troilite, and mackinawite (Table 4.1 and references therein) were easily attributable to contrasts in temperature and sulphur fugacity during each mineralisation's crystallisation. That simple view provided a base that would be useful for determining conditions of deposition while techniques for experimentally evaluating sulphur fugacity were just being developed. Maybe more intriguing than the mineralogy alone were questions on the controls of crystallographic habits and the textures of these abundant



iron sulphides; few viable hypotheses had been proposed by 1950 for processes that potentially could produce the different forms found in nature, as in Figure 4.4. For example, why does pyrite occur within specific areas and parageneses of mineral deposits consistently as cubes, pyritohedra, octahedral or framboids, but rarely as needles? Some success was achieved during the post 50s decades in resolving the nature of these morphological characteristics and their implications for hydrothermal crystallisation mechanisms and pathways. That success began with a necessary background on the stabilities of these minerals. Let's follow, from about 1950, the improving state of understanding of the stabilities of these most informative minerals, the iron sulphides.

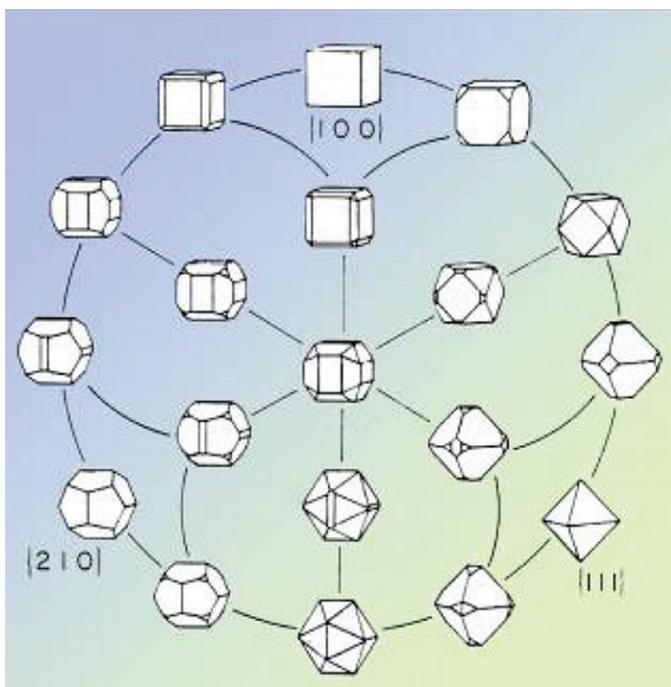


Figure 4.4 Forms of pyrite in nature (modified from Sunagawa, 1957).

Phase Relations. The first stage in resolving ore genesis was to develop an understanding of sulphide mineral stabilities from experimentally derived phase relations. Compiled in Table 4.1 are both early and more recent phase data for the iron sulphides.



Table 4.1 Iron sulphide compositions, structures, and thermal behaviour.

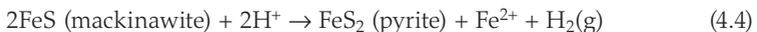
	Composition		Crystallography		T Limits, °C*
	Nominal	Atomic % Fe	Symmetry	Space Group (1)	
Pyrite	FeS ₂	33.29	cubic	<i>Pa3</i>	743 (2)
Marcasite	FeS ₂	33.4-33.5	hexagonal	<i>Pnmm</i>	<150 (3)
Greigite	Fe ₃ S ₄	42.8	cubic	<i>Fd3m</i>	<60 (4)
Smythite	Fe ₉ S ₁₁	45.0	rhombic	<i>R3m</i>	<53 (5)
Pyrrhotite	Fe ₇ S ₈	46.7	monoclinic	<i>F12/d1</i>	251 (6)
Pyrrhotite	Fe ₉ S ₁₀	47.4	hexagonal	–	282 (7)
Pyrrhotite	Fe ₁₀ S ₁₁	47.6	hexagonal	–	- (7)
Pyrrhotite	Fe ₁₁ S ₁₂	47.8	hexagonal	<i>F1d1</i>	- (7)
Troilite	FeS	50.0	hexagonal	<i>P6̄2c</i>	138 (8)
Cubic FeS	FeS	50.0	cubic	–	< 92 (9)
Mackinawite	FeS	52.9	tetragonal	<i>P4/nmm</i>	<70 (10)

*Approximate upper temperature limits to persistence for years. These soft, kinetic limits are approximate, so are indicated by the “<” symbol, in contrast to established thermodynamic limits, *i.e.* invariant points.

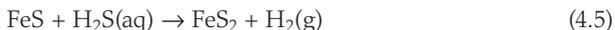
- (1) Gaines *et al.*, 1997; Mackovik, 2006
- (2) Barton and Skinner, 1967
- (3) Murowchick and Barnes, 1986b; Schoonen and Barnes, 1991; Rakovan *et al.*, 1995
- (4) Hunger and Benning, 2007
- (5) Furukawa and Barnes, 1996
- (6) Kissin, 1974; note that pyrrhotite is not an ideal solid solution
- (7) Kissin, 1974
- (8) Toulmin and Barton, 1964
- (9) Murowchick and Barnes, 1986a; not found in nature due to its instability
- (10) Benning *et al.*, 2000b; Rickard, 2012; Csákerényi-Malasics *et al.*, 2012

These phases are also shown in Figure 4.5, a somewhat simplified diagram, especially for the lower temperatures.

Further details can be found in *Michael Fleet's* comprehensive review for both low and higher temperatures (Fleet, 2006). The intent for Figure 4.5 is to give an overview and easy estimates of the thermal regimes implicit in the crystallisation of each of the binary iron sulphides of a mineral assemblage. The reaction paths among these sulphides are shown schematically in Figure 4.6 and discussed here. For those reaction paths, the percent molar volume changes for the replacement reactions may be written to be either positive or negative. If a reaction is written with stoichiometric loss of ferrous iron, for example:



for molar volumes of 20.49 cc/mole of mackinawite and 23.95 cc/mole of pyrite, there is a 41.57% volume *decrease* between the solids. In contrast, a sulphidation reaction for the same minerals:



entails a molar volume change of +16.89 % of mackinawite, a large *increase* that supports armoring which suppresses the kinetics of that reaction as illustrated by Figure 4.6. All of the reactions in Figure 4.7 proceed through loss of ferrous iron. Furthermore, in addition to reaction 4.4, these reactions all have decreasing molar volumes and sulphidation reactions, as with reaction 4.5, advance via an increase in molar volume.

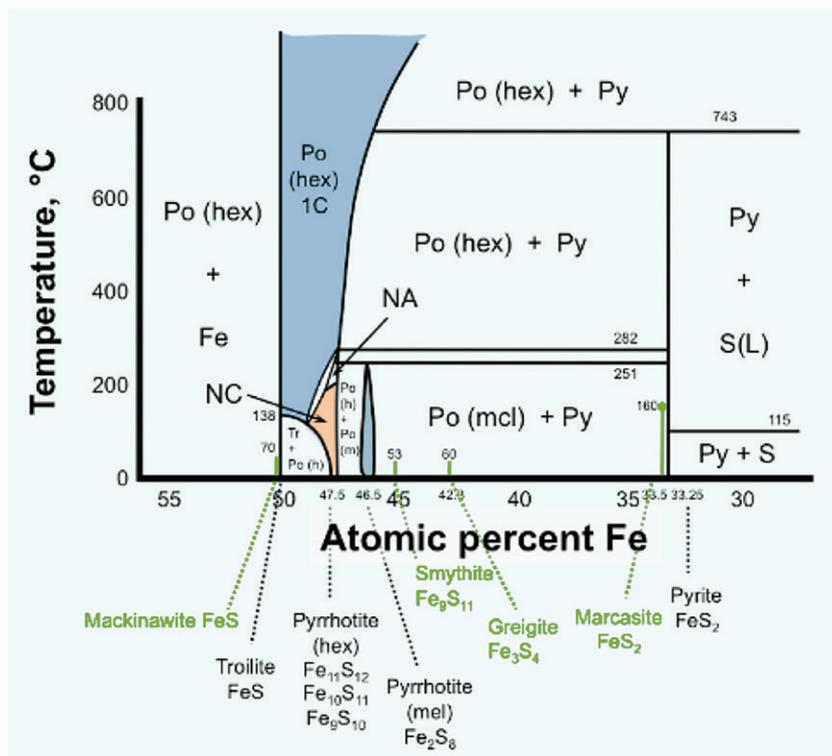


Figure 4.5 Thermal stabilities of the iron sulphides. Metastable minerals are identified in green together with the approximate highest temperatures at which rates of dissociation are still slow enough to permit a multi-year persistence. Thermodynamically stable phases are shown in black. NC (in orange) indicates a phase with non-integral repeat of the cell's C dimension and NA is the same for the A dimension. See Table 4.1 for sources of the data that underlie this figure.



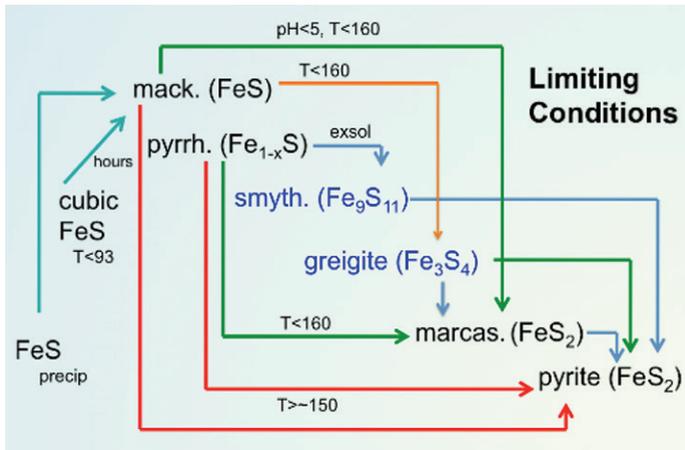


Figure 4.6

Reaction paths known among the iron sulphides. See the text for explanations of the conditions where these processes may occur and Figure 4.7 for the volume changes between these minerals that result from these reactions (modified from an initial compilation done with *Liane G. Benning* during her tenure at Penn State University, 1997).

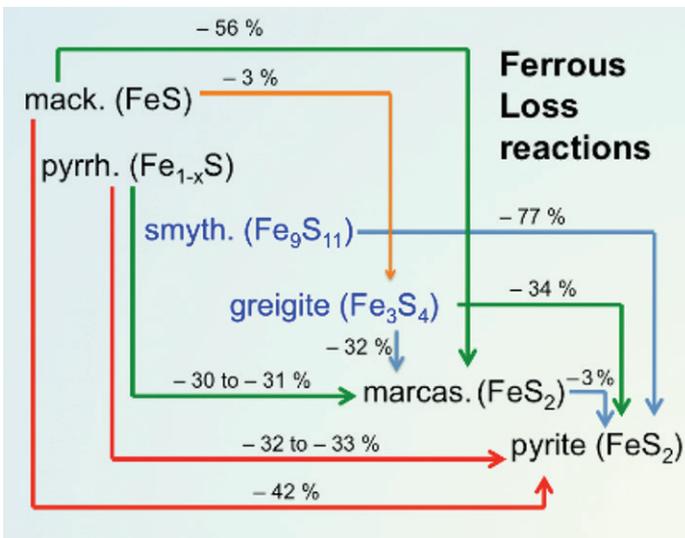


Figure 4.7

Changes in molar volumes by replacement reactions between pairs of iron sulphides (after an initial compilation done with *Liane G. Benning*, Penn State University, 1997).



Mackinawite and Greigite. In a general sense, the redox state during ore deposition changes across Figure 4.5, from very reduced with mackinawite present (comparatively elevated hydrogen pressure; Kishima, 1989; Wilkin and Barnes, 1996) to moderately reduced with pyrite.

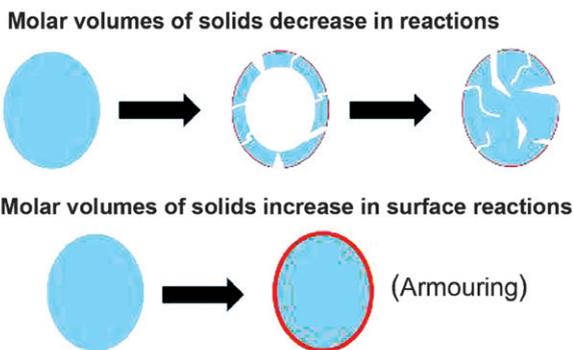


Figure 4.8 Textural effects of contrasting molar volume changes during replacement reactions.

Although mackinawite was identified only as recently as 1964 (Evans *et al.*, 1964), it is common in anoxic sediments and low temperature hydrothermal alteration (Berner, 1967; Rickard, 2012). Reaction paths that produce mackinawite are now thought to follow in general a rapid and complicated sequence of reactions, which neglecting hydration state, are first:



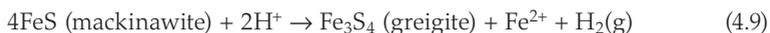
next is cluster formation in solution (Rickard and Luther, 2006):



and then fast particle nucleation (Jeong *et al.*, 2008; Csákberényi-Malasics *et al.*, 2012):



by which these solids quickly and progressively grow to larger and more ordered mackinawite particles (Wolthers *et al.*, 2003). These persist only if cool, $< -70^\circ\text{C}$. If warmer they react quickly into greigite, free ferrous iron and hydrogen, both of which have been detected as products of this process (Wilkin and Barnes, 1996; Benning *et al.*, 2000b; Cahill *et al.*, 2000; Hunger and Benning, 2007):

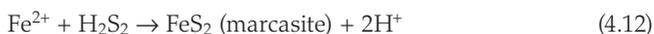


Greigite reacts to form pyrite unless below $\sim 60^\circ\text{C}$. The sequence of reactions (4.6) – (4.9) is important for the appreciation of the growth and persistence of metastable greigite (Pearce *et al.*, 2006). Being ferromagnetic, it is the principal basis for palaeomagnetic stratigraphy (Kodama, 2012).



Smythite. Smythite occurs as a product forming by one of three different paths: by siderite (FeCO_3) replacement, by exsolution from S-rich, 1C pyrrhotite, especially in nickel ores (Furukawa and Barnes, 1996) or as an alteration product from mackinawite or greigite (Krupp, 1994). Apparently, it nucleates easily but is kinetically preempted where pyrite nuclei are present. The upper stability limit for smythite, suggested to be 53°C , was derived from siderite transformation experiments and the transformation from precursors pyrrhotite, mackinawite, or greigite has been approximated to be less than 65°C (Krupp, 1994).

Marcasite. Stability limits for marcasite are of considerable interest because of its common occurrence in a variety of mineral deposits and its value as an indicator of crystallisation conditions. Hydrothermal experiments have revealed that it will precipitate from protonated polysulphide solutions at pHs only below 5.0 and temperatures held under 150°C (Murowchick and Barnes, 1986b). At higher temperatures or pHs, pyrite forms instead. This sensitivity to acidity had long been discovered and described by Allen *et al.* (1914) but the reasons for this effect had to wait until measurements were made of the ionisation constants of the aqueous polysulphide species, H_2S_x (Meyer *et al.*, 1977):



and the structures of the polysulphide species and marcasite had been determined (Murowchick and Barnes, 1986b).

Marcasite is common in a wide variety of deposits including submarine vents, roll-front uranium ores, epithermal precious metal ores, and Mississippi Valley type ores, often in euhedral forms, presumably due to reactions of ferrous and polysulphide species. It has a signature cockscomb form. However, in Mississippi Valley ores, this form is observed but is found by X-ray examination to now be pyrite that has apparently replaced the initial marcasite. In such cases, the X-ray peaks tend to be broad, supporting the inference that the mineral was initially marcasite but that the replacement process left some disorder and had not completely recrystallised the iron sulphide.

There is a second family of marcasites that formed by replacement processes, especially from pyrrhotite. Of course, the resulting morphology follows that of the initial pyrrhotite and is not cockscomb type. Again the upper temperature limit of 150°C seems to hold for the marcasite structure to be able to persist for years (Murowchick and Barnes, 1986b).

Pyrite. It is the earth's most abundant sulphide partly due to its stability and from its crystallisation by replacement of other common minerals of the Fe-S binary under even slightly oxidising conditions (Benning *et al.*, 2000b). In highly reducing conditions, growth does not take place by reactions involving the other binary sulphides. Reaction paths with H_2S , HS^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , $\text{S}_4\text{O}_7^{2-}$ or organic sulphonates or cysteine do not produce pyrite. Instead, with such solutions, its



nucleation is kinetically favoured by polysulphide-forming solutions at saturation even at temperatures as low as 70°C (Wilkin and Barnes, 1996) but with slight pyrite undersaturation, smythite nucleates instead (Furukawa and Barnes, 1996).

Pyrite is so common that its textural characteristics are especially valuable for deciphering depositional conditions, particularly because of the large variety of its morphological forms in hydrothermal environments. These deserve our special attention. In about 1960, Amstutz (1963) and Sunagawa (1957) reported that in ore deposits known to them there were areas with consistent distributions of one or more habits of pyrite as cubes, pyritohedra, or octahedral (Fig 4.4). Since then, those observations have been reported often in the mineral deposits

literature. Being intrigued, we proposed that once nucleated, the morphology could well be governed by the kinetics of crystal growth (Lasaga, 1998). If so, experiments at controlled temperatures and degree of saturation during growth could reveal the conditions favouring each of the different forms. During his doctoral thesis research, *Jim Murowchick* grew hydrothermally six different forms of pyrite: needles, dendrites, cubes, pyritohedra, octahedra, and anhedral with the observed surface roughness varying from smooth to heavily striated (Murowchick and Barnes, 1987). In the schematic Figure 4.9, the effects of temperature and supersaturation show that at 250°C and low supersaturation (growth gradient of 0.35°C/cm), pyrite needles grew. At both a mean temperature of 450°C and higher supersaturation (4.6°C/cm), cubes grew, and with progressively higher supersaturations, octahedra crystallised, then pyritohedra, then dendrites, and finally anhedral masses grew at extreme supersaturation (Fig. 4.9). Apparently, pyrite's habits indicate relative saturation levels of concentrations in the depositing

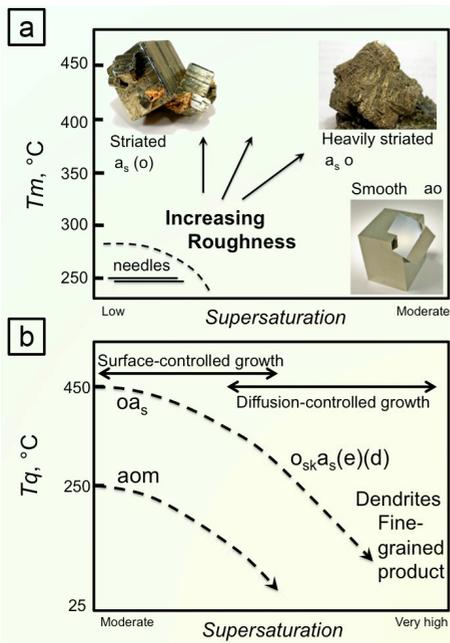


Figure 4.9 Effects on pyrite morphology and striation density of combined temperature and solution supersaturation during hydrothermal growth. (a) T_m is the mean temperature during growth. (b) T_q is the initial quench temperature and the dashed line is the nominal cooling path (modified from Murowchick and Barnes, 1987, Fig. 4). Forms in order of development are $\bar{a} = \{100\}$, $o = \{111\}$, $e = \{210\}$ $m = \{311\}$, and $d = \{110\}$. Subscripts s and k indicate striated or skeletal forms. (x) = minor forms.



hydrothermal solution. Because the striation density on the pyrite surfaces changed from virtually none at 250°C to extreme at 450°C, that may be an easy means for roughly estimating pyrite deposition temperatures. Photographs of crystals grown under these conditions are found in Figures 4.10 and 4.11.

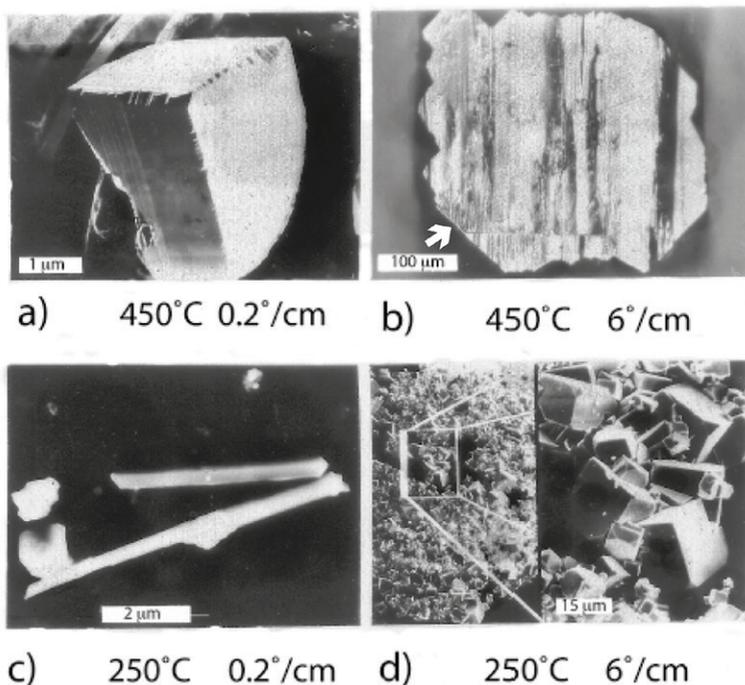


Figure 4.10 Pyrite crystals grown under steady-state conditions. (a) A weakly striated cube from a mean temperature of 450°C at a low supersaturation gradient of 0.8°C/cm. (b) A heavily striated cube grown at a mean of 450°C with a moderate supersaturation gradient of 4.6°C/cm. A horizontal cube face extends from the tip of the arrow at a {111} face. (c) Needles from a mean of 250°C and low supersaturation of 0.35°C/cm. (d) Striation-free cubes with many {111} faces from a mean of 250°C and moderate supersaturation at 6.2°C/cm (from Murowchick and Barnes, 1987).

The acicular pyrite crystals that formed experimentally near or below 250°C at low degrees of supersaturation are comparatively rare in nature. Examples occur in sulphide veins of the Appalachians and few other locations (Murowchick and Barnes, 1987; Hammarstrom *et al.*, 2005). An unsolved question is why is that form of pyrite so rare? The striations on the pyrite surfaces reflect the physical state (crystal structure, dislocation density, twin formation) as well as the chemical conditions of formation of the host crystal (*i.e.* temperature, saturation state of growth conditions and mechanisms of formation). In many mine

samples, pyrite cubes were found by Owsley (1998) to have more regular widths of their striations than those on pyritohedra but with widths of both varied over 5–60 μm (see also Benning *et al.*, 2000a). For a more complete understanding of their crystallisation processes, recent tools such as molecular dynamic mocerlling and kinetic Monte Carlo techniques, can become aids to correlate these data to interpret the crystallisation conditions of the striations forms. *Ab initio* models can now provide accurate potential surfaces to understand bond formation and bond rupture as developed by several geochemists (*e.g.*, Lasaga, 1998).

Examples of pyrites and their deduced conditions of growth are illustrated below by Figures 4.11 – 4.13. Further investigation of these observations could be beneficially field-tested by correlations of pyrite habits with fluid inclusion-based temperatures and solution concentrations.

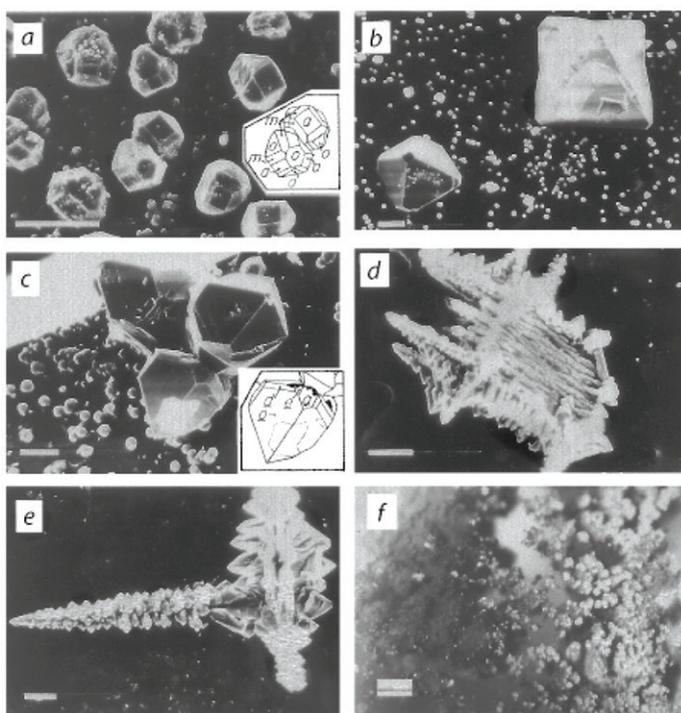
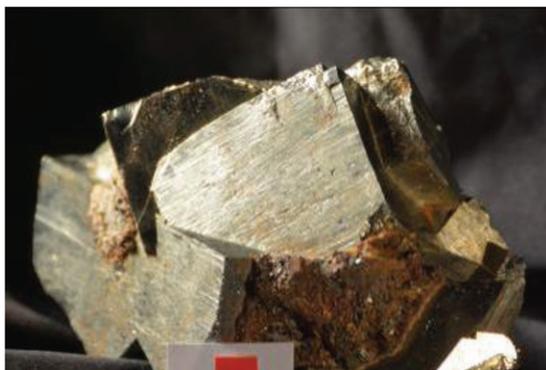


Figure 4.11

Pyrite crystals grown by quenching that caused supersaturation. Extent of supersaturation increased from (a) through (f) by cooling to room temperature from 250°C in (a) and from 400–450°C in the others. The following forms are observed: (a) crystals with $a=\{100\}$, $o=\{111\}$, and $m=\{311\}$ faces (b) octahedra (c) skeletal octahedra with $a=\{100\}$, $e=\{210\}$, and $d=\{110\}$ faces (d) dendritic growth on earlier cube (e) dendrites and (f) grains without evident crystal faces (from Murowchick and Barnes, 1987).





Photograph by Charles Miller, #31.580, 2014.

Figure 4.12 A pyrite sample with twinned cubes and slightly striated surfaces. The red bar is 1 cm long. From Niccioletta Mine, Tuscany, Italy. See Table 4.2 for textural implications.



Photograph by Charles Miller, #31.582, 2014.

Figure 4.13 A pyrite sample with twinned pyritohedra and heavily striated surfaces. The red bar is 1 cm long. From Minas Gerais, Brazil. See Table 4.2 for textural implications.

The approximations from *Bill Murowchick's* experiments provide bases for estimating the conditions under which pyrite was deposited hydrothermally. Included are both relative degrees of supersaturation and, semi-quantitatively, of temperature, as summarised in Table 4.2. Also, the sizes of pyrite crystals provide clues to the relative duration of times of deposition, the larger crystals clearly taking longer to form. Although none of these three criteria give quantitative information, they can add insight to field observations, such as where exploring for principal flow paths to guide exploration for prime mineralisation.



Inferences from two examples pictured in Figures 4.12 and 4.13 illustrate tentative applications of these models. (1) The large, 9 cm, twinned cubes of Figure 4.12 imply a relatively *long time of deposition*. The cubic habit indicates that there was comparatively *low supersaturation* of the hydrothermal carrier, and the low density of striations fits with experimental temperatures of about 250-300 °C. (2) The 6 cm pyritohedra of Figure 4.13 indicates a *high level of supersaturation* and, again being large, a relatively long time for crystallisation. Its highly developed striations fit with a deposition temperature of about 400 ± 50 °C.

Table 4.2 The Murowchick approximations, clues from pyrite morphologies.

Habit	Supersaturation	Striation Density	Temperature °C	Growth Mechanism
Acicular (needles; wires)	Very low	None	~250	Screw dislocation
Cubes	Low	Slight (increases with supersaturation and temperature)	~300	Surface-controlled layers
Octahedra	Moderate	Low	~350	Surface-controlled layers
Pyritohedra	High	High	~400	Surface-controlled layers
Dendrites	Very high		Intense quench	Diffusion-controlled supply
Anhedral	Extreme	None		

Through the 20th century, explanations were offered for only a few of the many forms of pyrite for processes that could favour their crystallisation. Those were mostly qualitative. More quantitative explanations are needed of the causes of crystallisation of the many other forms of pyrite that are illustrated by Figure 4.4, in addition to those examined here. Of considerable geochemical interest would be quantitative, kinetic reaction paths and rates for those many other forms because their occurrences are common enough that there could be frequent applications of an improved theory.

There is another very abundant family of pyrite forms found in the rock record, the framboids. Because their origins have been found not to be hydrothermal, but typically marine and sedimentary (Wilkin and Barnes, 1997a,b), they lie outside the range of topics of this issue of *Geochemical Perspectives*. The discussions presented to this stage are focused on the maturing of investigations during the second half of the 20th century into hydrothermal geochemistry, especially into the nature of hydrothermal ore-forming environments. In parallel with lab investigations, there were concomitant studies of natural hydrothermal systems, which also produced new concepts. I will next discuss the development and critical discoveries in these ancillary aspects, starting with active geothermal systems.



5.

GEOHERMAL SYSTEMS

Before about 1950, there were lingering doubts that geothermal systems (Fig. 5.1), both ancient and modern, were responsible for hydrothermal ore genesis. That uncertainty stimulated searches for evidence that could test for correlations between ore deposits and geothermal sites. The most accessible links would be with hydrothermal ores formed at the temperatures found commonly in many active, continental geothermal fields. Those earliest recognised were mercury-containing hot springs, such as the classic examples in the California Coast Ranges (White, 1981). Comparisons of the very similar characteristics of those hot springs and other mercury deposits are found in White (1967) and in the compilation that *Terry Seward* and I assembled in the late 1990s (Barnes and Seward, 1997). Comparable continental hot springs in Tuscany (Italy), Kamchatka, and New Zealand were also recognised to precipitate antimony- and/or arsenic-rich deposits (Dessau, 1952; Ozerova *et al.*, 1971; Krupp and Seward, 1987). These were important links between hydrothermal and geothermal processes and are shown as examples in Figures 5.2 for Tuscany and 5.3 for Kamchatka. In many of these active geothermal areas, the maximum metal concentrations of the geothermal fluids (Table 5.1) generally correlate well with the salinity of each system, suggesting halide complexing. The metal concentrations imply that important mineralisation can be precipitated by geothermal waters. The geothermal precipitates are up to ore grades for the eight elements noted in this table.

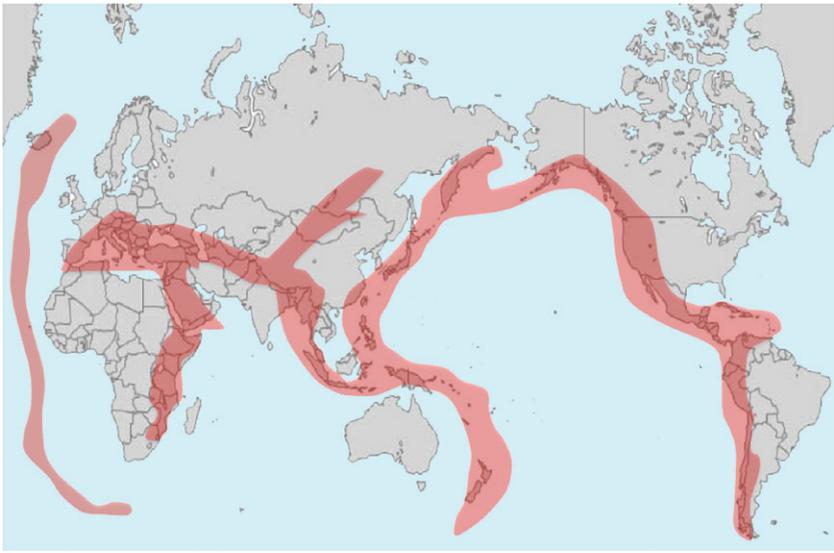


Figure 5.1 Global geothermal belts.



In 1995, the 8th International Symposium on Water-Rock Interaction held in Vladivostok, Russia, provided a rare opportunity with a post-meeting field trip to some of the most spectacular sites of Kamchatka. That wilderness region has 29 active volcanoes and multiple hydrothermal deposits and geothermal areas. Helicopter travel made possible examining several of these areas at the southeast tip of Kamchatka, especially Geysir Valley, where there were six geysers in action (Fig. 5.3). In the close-by Uzon Caldera, hot springs contained up to 30 ppm As and 0.1 ppm Hg (Okrugin, 1995) similar to the values in Table 5.1. A scene in August 1995, from further east at low elevation and about 54° North latitude, is shown on the back cover of this *Geochemical Perspectives* issue. As expected at this latitude, much of the higher interior central and northern regions were snow and glacier-covered. Given this climate, it was astonishing that palm trees were observed growing in the geothermally heated microenvironment of Geysir Valley. How could seeds have been brought there by nature to begin such alien vegetation among the glacial terrains?

Table 5.1

Maximum metal concentrations in solutions and in precipitates from 10 geothermal areas (in ppm or %; from Weissberg *et al.*, 1979; White, 1981; Simmons and Brown, 2007).

	Solutions	Precipitates
Ag	2.4	7 %
As	39.5	30.15 %
Au	23	85
Cu	8	2.5 %
Hg	0.12	7,000
Pb	102	3,000
Sb	1.2	10 %
Zn	540	3.4 %

Furthering the link between geothermal phenomena and hydrothermal ore formation are submarine geothermal systems of two types: first, black smokers. This was discovered to be a hydrothermal progenitor of massive sulphide deposits by a collaborative endeavour under the direction of my Penn State colleague, *Hiroshi Ohmoto* (Edmond *et al.*, 1979; Ohmoto and Skinner, 1983). These include the Kuroko type deposits, which are products of these submarine geothermal processes (Tatsumi, 1970; Galley *et al.*, 2007). A second type of submarine geothermal system, the deep sea hydrothermal sedimentary type, we also studied at Penn State (Pottorf and Barnes, 1983). For his doctorate *Bob Pottorf* (Pottorf, 1980) was offered drill cores that were collected during cruises to the Atlantis II Deep of the Red Sea in 1971 and 1972. We soon carried out a study of their



characteristics and of their implications for sulphide mineral deposition. The cores had been protected from oxidation by sealed pipes so were in pristine condition. They revealed veins of Cu-Fe-S minerals and their ore-grade concentrations in those cores demonstrated again that hydrothermal and geothermal processes and ore genesis are closely interrelated phenomena (Barrie and Hannington, 1999). This matched well the conclusions of Weissberg *et al.* (1979), who showed that geothermal waters may deposit at least 5 elements in amounts adequate to form epithermal ores, provided that high flow rates persist for millions of years. Once that conclusion was eventually accepted for at least the 8 elements of Table 5.1, further investigations of comparatively more readily accessible terrestrial geothermal systems became popular. Studies following from these conclusions were expected to help resolve some of the other enigmas of hydrothermal ore deposition, such as the causes and rates of ore precipitation. Let's consider the implications for the theory of epithermal ore genesis of those early accumulations of physical and geochemical characteristics of geothermal systems.

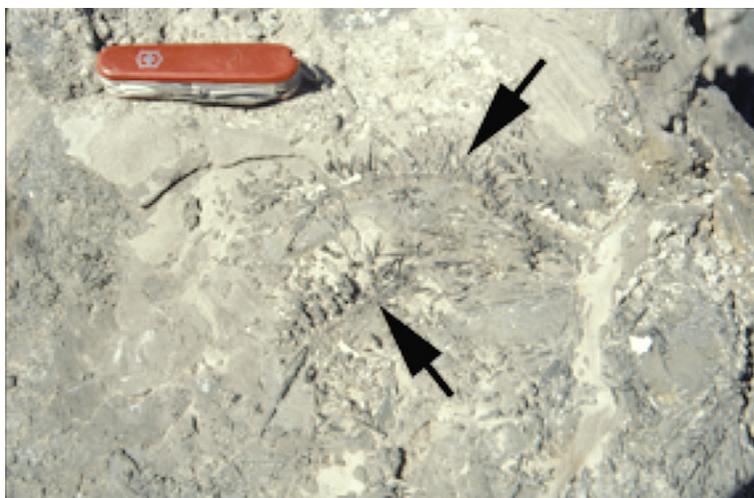


Figure 5.2 Stibnite crystals (pencil-shaped) in a hot spring of the Tafone Antimony Mine in Tuscany, Italy.

Until about 1950, the principal emphasis of investigations of geothermal systems was on exploration for heat recovery. That outlook broadened in the next two decades, led by investigations by scientists of the Chemistry Division of the Department of Scientific and Industrial Research in New Zealand. Among the major contributors were *Jim Ellis*, *Werner Giggenbach*, *Tony Mahon* and *Terry Seward* whose research was focused first on the many geothermal fields of New Zealand (*e.g.*, Wairakei, and Kawerau see Fig. 5.4 and 5.8) but also covered much of the earth's other geothermal areas (*e.g.*, Ellis and Mahon, 1977 and Chapters

14-17 in Barnes, 1997; and exemplified by the photographs of Nesjarellir, Iceland in Fig. 5.6 and Cerro Prieto, Mexico in Fig. 5.7). The prototypical example of a geothermal system became the Wairakei geothermal field in New Zealand (Fig. 5.4) both because of its early prominence and importantly, as a result of the depth and number of studies published on it, notably by Ellis and Mahon (1977) and Elder (1981). Consequently, a summary of its characteristics as the archetype of geothermal systems seems worthwhile here, to see what they reveal about ore depositing processes.



Figure 5.3 Geyser Valley, Kamchatka where thermal springs are depositing As-, Hg-, and Sb- sulphides and which are drained by a 1 metre-wide stream in the centre of this photograph. See Ozerova *et al.* (1971) for details.

5.1 Wairakei, New Zealand

Outflows from geysers and hot springs, both here and in many other examples, were found to be intermittent in time and location. This behaviour is caused by gradual sealing of the active flow channels by wall rock alteration or by precipitates, such as by silica coatings. These processes shrunk the local permeability, causing the outflow to move laterally from site to site within geothermal fields. Evidence of such local migration is obvious because areas with active hot springs are typically tens of metres across, sometimes enclosing dying vegetation that dates the local outflow as quite recent. Furthermore, interspersed amongst the active springs are low-flow areas with fossil springs, usually without vegetation, which had died off long ago. Flow at such sites may be cyclical, gradually decreasing to a minimum as sealing develops then renewed by tectonic activity



which cracks open both old, sealed channels and newly generated channels. Together, they reestablish the local flow rates. A time cycle of local flow rates from minimum to maximum may last roughly 5,000 years, as seen at Wairakei (Ellis and Mahon, 1977) or thousands to tens of thousands of years elsewhere in the Taupo Volcanic zone around Wairakei (Kohn and Topping, 1978; Houghton *et al.*, 1995). These cycles are short compared to the life of the total Wairakei System, where geothermal activity has persisted for 0.5 Ma as measured by K/Ar dating of hydrothermal alteration (Ellis and Mahon, 1977). Other geothermal systems persisted for the long periods noted in Table 5.2.



Figure 5.4 Collecting lines for steam from geothermal wells at Wairakei, New Zealand in 1976.

Table 5.2 Duration of some modern geothermal systems, in millennia.

East Mesa, California	10
Cerro Prieto, Mexico	10
Great Geysir, Iceland	>10
Salton Sea, California	>100
Wairakei, New Zealand	500
Broadlands, New Zealand	500
Steamboat Springs, Nevada	1,000

Ellis and Mahon (1977); Polster and Barnes (1994); McKibben and Hardie (1997)





Figure 5.5 The casing of Salton Sea Well IID #1 after 5 weeks of geothermal fluid flow. The scale is primarily of silica, a 7 cm-thick layer inside the 20 cm pipe. This well, costing about \$1 million, was geothermally useless due to its low permeability caused by the thick scaling. Allowing free flow with little back pressure to control scaling was an expensive blunder.

Clogging is the main problem that causes decreased permeability both in geothermal wells and host rock sources, arising from the deposition of armouring silica or carbonates. For example, the concentration of silica at the perimeter of the pipe in Figure 5.5 reflects the flow distribution as the hot fluids rise. It is well understood that the hydrothermal solutions spiral upward along the walls of the pipe while both boiling and releasing dissolved gases. These peripheral liquids move slower than the gases which move upward along the axis. When we (with *Don Rimstidt* and *Bill Downs*) added H_2S to an online experiment at the Salton Sea area (Barnes *et al.*, 1978), noted were no precipitates of the metals from the fluids because the gas phase was partitioned into axial flow without reacting with the metal-carrying liquid (Arthur, 1983). The same effect occurred when aqueous NaHS was inserted because it very quickly reacted to free more H_2S that rose again axially at relatively high velocity without causing sulphide precipitation. No wonder veins fill inward from the walls and the gases separate to rise along the core of the vein opening.

We have shown that the temperatures of geothermal reservoirs are typically 120 – 370 °C and always below 400 °C (Polster and Barnes, 1994). These temperatures agree exactly with data on epithermal ore deposits as compiled by Hayba (1983) for 3387 fluid inclusion measurements at 140 – 400 °C, averaging 240 °C. The match between these two sets of measurements further supports the inference that they are identical phenomena.



Table 5.3 The nature of some geothermal systems.

	Wairakei, New Zealand	Rift Valley Types
Developed for heat:	1953	
Area:	50 km ²	0-150 km ²
Dominant water source:	meteoric water	meteoric water
Recharge time or distance:	10,000 yr water age	60-80 km typical distance
Well production depth:	800 m average	usually 600-800 m
Production temperature:	240-280°C	120-370°C
Thermal gradients:		15-80°C/km
Reservoir depth:	2,000 m maximum	600-800 m typical
Reservoir volume:	100 km ³	x-x00 km ³
Porosity:	10 % average	10-20 % averages
Permeability, md:	100	0.1-600 typical
Flow cycles:	5,000 years	with fast flow, 10 ² -10 ³ years slow flow, 10 ⁴ -10 ⁵
Solution volume:	10 km ³	
Deep water residence time	10,000 yr	
Discharge:	400 l/sec 0.014 km ³ /yr = 10 ¹⁰ kg/yr 5,000 km ³ in 0.5 myr	4x10 ⁻⁵ – 5x10 ⁻³ km ³ /yr (similar in Fig. 5.7)
Heat flow:	1,000 ± 100 MW	
Age, years:	500,000	10,000-1,000,000
References	Cathles (1977); Ellis and Mahon (1977); Elder (1981)	Polster and Barnes (1994); Barnes (2000)

Powering of geothermal systems depends upon the heat input from igneous intrusions. That input must continue for the known lifetimes of such systems (Table 5.2) extending often to 0.5-1.0 million years. These times are roughly identical to the lifetimes of well dated hydrothermal ore deposits which often had deposition persisting for 1 million years and sometimes even up to 3 million years (Sillitoe, 1994). However, these lifetimes are far longer than an intrusive cooling lifetime as determined by Cathles (1977) to be about 25,000 years for a typical-sized intrusive (<3 km diameter). *Larry's* calculated age intervals are based on evaluating each of the several heat-dissipating processes, especially conduction and fluid convection (Norton and Cathles, 1979). Therefore, multiple intrusions are required to heat a geothermal system for up to a few millions years.





Figure 5.6 Discharge from the hottest of geothermal wells at 380 °C in the Nesjarellir Geothermal Field, Iceland. Such extreme temperatures in Icelandic wells are described by Aanórsson (1995). Pressures in this well were extreme, making valve control difficult so the flow here is unconstrained.



Figure 5.7 Thunderous waste water discharge of 700 metric tons/hour from the Cerro Prieto, Mexico power plant in 1975. The flow rate is fast enough that there is no important silica precipitation until the stream reaches the milky impoundment at the left.

Furthermore, those plutons must be close enough together in time, probably less than 25,000 years apart, if hydrothermal flows are to be continuous. They must also be concentrated spatially, probably at less than about a kilometre separation, to cause cumulative hydrothermal transport and concentrated deposition (Barnes, 2000). Therefore, about 20 intrusions are required per geothermal system if each pluton is to contribute as a heat engine to maintain hydrothermal processes for 500,000 years as at Wairakei (Table 5.3). That much igneous activity is not easily accommodated within such a confined area and with persisting time continuity. This problem deserves further investigation and better modelling.

Industrial development of geothermal systems is illustrated by Figures 5.4, 5.7 and 5.8. Processes involved are the collection of steam from multiple wells, the wellhead separation of steam for power generation, and the disposal of the liquid discharge. The separation system is quite similar in different geothermal fields, as is the collection piping but the discharge procedure varies considerably. Reinjection of the fluid output has become more common, as it has been found to extend the life and practical thermal output of a geothermal field. It also avoids local pollution by the solutes content and acidity of the discharge.





Figure 5.8 A geothermal well at Kawerau, New Zealand. The tower in the centre of the picture is to separate steam for power generation from the residual hot water flow. The rusty tower to the left with the large steam plume is a silencer and cooler for the rejected hot water flow.

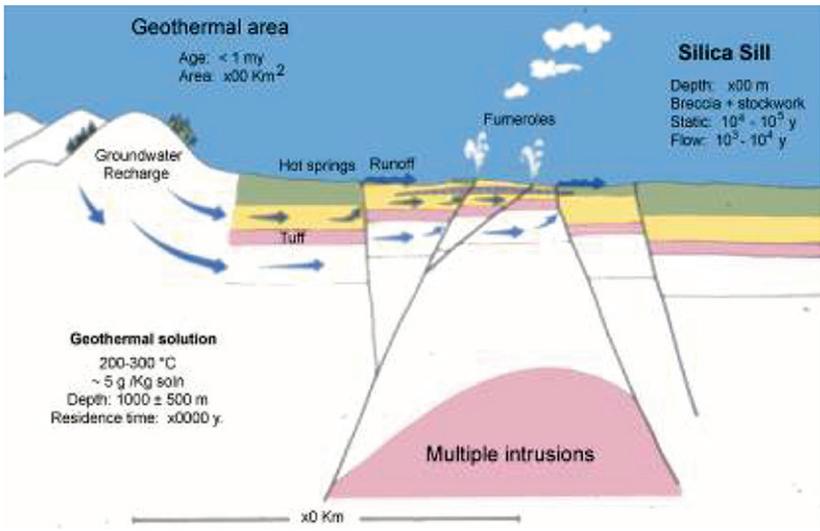


Figure 5.9 A schematic cross section of a representative geothermal system.

The nature of typical geothermal systems is summarised in Figure 5.9. Of particular interest is that the subsurface hot plume of hydrothermal flow is displaced downstream from the heat source, a pluton. There are many examples of this flow pattern, such as in the several geothermal sites in the Imperial Valley of California, south of the Salton Sea (McKibben and Hardie, 1997). Of course, this implies that hydrothermal alteration and mineralisation should not be concentrated centrosymmetrically around the powering intrusive but warped to varying extents in the downstream direction of meteoric water flow. Prospecting could depend on recognising this geometry whether searching for ores or for more calories. This also explains why drilling deeper in geothermal systems may commonly find cooler waters rather than an expected temperature increase because the intrusion may be upstream of the near surface hot waters being exploited.



Among the commonest, cooler hydrothermal ores is the Mississippi Valley Type, the source of about 25% of the world's commercial zinc and lead (Leach *et al.*, 2010). These deposits are amenable to experimental and theoretical investigations, especially using thermodynamics, because they generally formed between 50 and 200°C (Sicree and Barnes, 1996). Consequently, Mississippi Valley-type (MVT) deposits became early targets of our group (Barnes, 1959) as we hoped to unravel their origins by using continuing advances in understanding of hydrothermal processes. Let's begin by elaborating on the early discovered MVT characteristics. The range of structural and tectonic settings of larger examples of MVT deposits are summarised in Table 6.1. Apparently, epigenetic MVT's are much more common than syngenetic examples, the latter forming at the surface contemporaneously with the enclosing host rocks. Often the epigenetic ores are found near the margins of large palaeobasins thought to have been deeper than 3 km and located typically within 30° of the equator during ore formation. Those environments imply that fluid sources had been tropical, marine, algal, phytoplanktonic and evaporitic. The normally highly saline compositions of the ore's fluid inclusions agree with such basinal sources. MVT host rocks are predominantly carbonates, typically of Phanerozoic ages, and devoid of igneous rocks (neglecting those with recoverable fluorite).

6.1 The Upper Mississippi Valley District (UMVT)

The archetypical MVT deposit, where we chose to concentrate our study, was the Illinois Iowa-Wisconsin District. This covers an area of 10,000 km² with over 100 million tons of ore production averaging about 5 wt% zinc and 0.5 wt% lead, that earned over \$1 billion in the last half of the 20th century. There were several geological and geochemical reasons for our choice. First, there was available a large and diverse literature including, as a geological base, a superb, detailed opus by Heyl *et al.*, U.S. Geological Survey Professional Paper 309 (1959). Also, this district is free of post-ore metamorphism, significant deformation, or obliterating weathering. Its structural setting is the commonest for MVTs as shown by Table 6.1.

Chronology. The timing of Upper Mississippi Valley Type (UMVT) sulphide deposition has been determined, with consistent results from Rb-Sr isochrons of three sphalerite bands, to be 270 ± 4 Ma. Furthermore, in these settings the galena proportion increased over sphalerite in the upper, younger bands (Brannon *et al.*, 1992). This study found that sulphide deposition had ended before four calcite stages occurred about 100 Ma later. The uplift of the Alleghenian orogeny of the southern Appalachians occurred between 250 and 320 Ma and was contemporaneous with the sphalerite ages. These ages were discussed



in detail by Garven *et al.* (1993). The immediate implication was that the rising of the southern Appalachians had provided an elevation for gravity-driven water flow toward the northwest into the Illinois Basin, then through the basin with outflow to the northwest through the Illinois – Iowa – Wisconsin ore district. Figure 6.1 reveals that the distances of fluid flow are long.

Table 6.1 The structural setting of Mississippi Valley Type deposits.

Cratonic Deposits: always epigenetic	
Illinois-Iowa-Wisconsin Laisvall, Sweden Nanasivik, Baffin Island, Canada North Pennine Field, England	Silesia, Poland Southeast Missouri Tri-state: Oklahoma-Kansas-Missouri Viburnum Trend, Missouri
Hinge Zone Deposits: many in reefs	
Epigenetic Appalachia Caledonia Belt, Europe Daniels Harbor, Newfoundland, Canada Gays River, Nova Scotia, Canada Pine Point, Northwest Territories, Canada Reef Ridge, Alaska	Syngenetic Mezica, Yugoslavia
Basin Floor Deposits: always syngenetic	
Bleiberg, Austria Mirgalimsai, Kazakhstan	

The path beginning in the uplifted mountains northward and to the edge of the Illinois Basin is roughly 400 km, then another 400 km through the basin and, finally 300 km more to ore deposition in the District. That these distances are reasonable was demonstrated by detailed hydrodynamic and thermal modelling of such flow by *Craig Bethke* (Bethke 1986), then *Grant Garven* and colleagues (Garven *et al.*, 1993), and finally by Rowan and Goldhaber (1995, 1996) with a remarkable consensus. An example of the flow modelling, as represented by Figure 6.2, shows the northward flow that was apparently caused by the Alleghenian Uplift of the southern Appalachians (see arrows in Fig. 6.2). For the observed ore-depositing temperatures of the district to be controlled by the outflow from the Illinois Basin, the input into the basin had to have a groundwater inflow velocity near 11.3 m/a. That flow had a heat input from the deep crust and mantle. The heat was collected first by its downflow into the south end of the basin where models evaluated it to be 4.3 heat flow units (hfu) grading to 1.5 hfu in the upflow region at the north end. Gravity-driven outflow was constrained to best fit the geography by a 5:1 lateral convergence northward toward the district. Note that the peak temperature shown by Figure 6.2 is only near 100 °C (Bethke, 1986). This temperature is much less than the maximum that was evaluated by several local



geothermometers to be above 200°C. This will be discussed below. The calculations by Garven *et al.* (1993) for water flow rates at 1 – 5 m/a give a slightly higher outflow transient temperature of 150°C, still too low compared to palaeotemperatures of over 200°C. Rowan and Goldhaber (1995) resolve this thermal problem by proposing higher thermal input into the Illinois Basin by more warming through increased igneous activity in the southern part of the basin. There are several lines of evidence to support extensive, contemporaneous igneous activity in the southern end of the basin at sites surrounding Hicks Dome (Fig. 6.3). Such igneous activity was dated with average Ar-Ar age of 271.3 ± 0.6 Ma, effectively the same age as ore deposition at 270 ± 4 Ma (Rowan and Goldhaber, 1996). Another source of supplemental heat could be from radiogenic decay of the exceptionally high uranium contents (45 ppm), of the underlying Precambrian basement (Spirakis, 1995; Spirakis and Heyl, 1995).

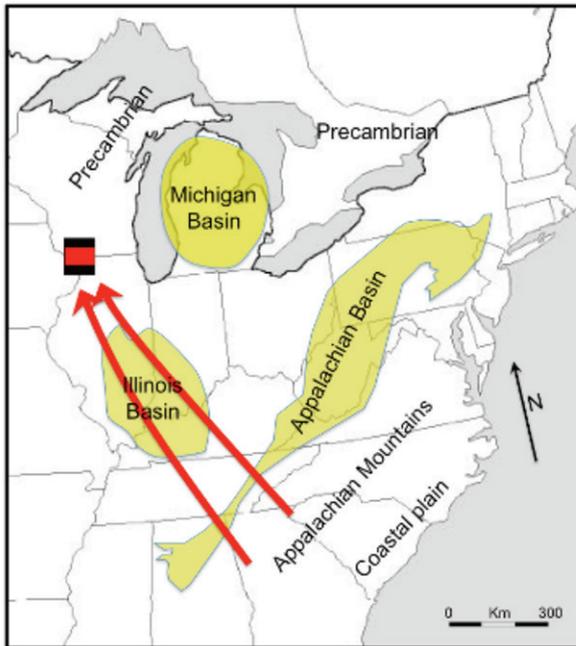


Figure 6.1 Modelled water flow from the elevated southern Appalachians through the Illinois Basin to the Upper Mississippi Valley Ore District (redrawn after Bethke, 1986).



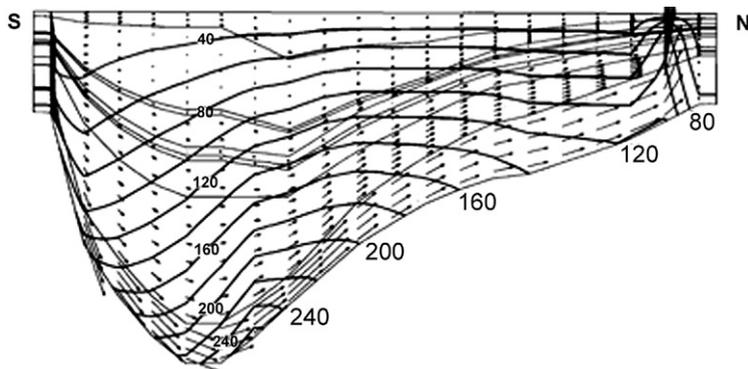


Figure 6.2 Water flow vectors (small arrows) and temperature contours (20°C intervals) representing late Permian hydrothermal outflow from the Illinois basin. The section starts from the southern Pascola Arch (left end) and ranges 700 km northward to the ore district (right end). The stratigraphic boundaries show the 9 different beds in the basin and span the time periods between the Cambrian and the Permian (modified from Bethke, 1986, Fig. 11e).

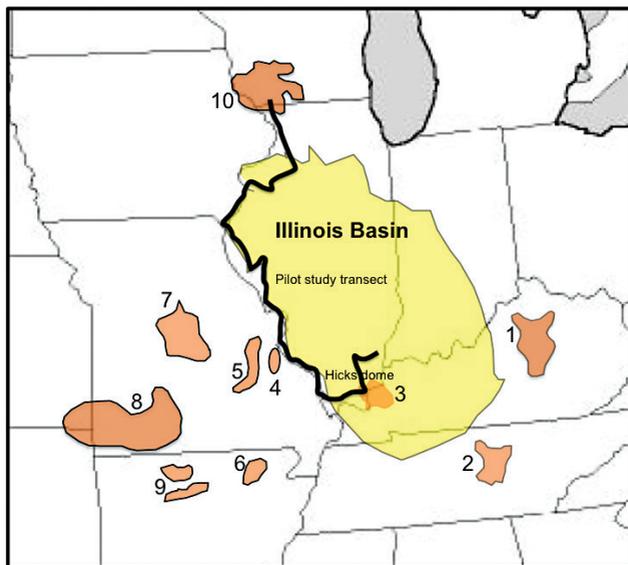


Figure 6.3 Location of drill holes (black line) of the Pilot Study Transect from the Illinois Basin Hicks Dome (marked as 3), to the Upper Mississippi Valley District (shown as 10). Other nearby MVT districts: 1: Central Kentucky; 2: Central Tennessee; 3: Illinois-Kentucky; 4: Old Lead Belt; 5: Viburnum; 6: Northeast Arkansas; 7: Central Missouri; 8: Tri-State; 9: Northern Arkansas (modified from Erickson *et al.*, 1987).



Hydrology. There is corroborating, independent evidence supporting the general agreement on the above modelling of the flow through the Illinois Basin (Erickson *et al.*, 1987). The confirming argument is based on trace Zn and Pb distributions in a fence of 13 deep holes drilled along the west centre of the Basin (Fig. 6.3). Anomalous trace metal concentrations were identified to be those above 200 ppm Zn or 100 ppm Pb in analyses of the sediments in the stratigraphic horizons shown in Table 6.2. Such high values were very rare in the Illinois Basin with the exceptions of the horizons just above the St. Peter sandstone (Erickson *et al.*, 1987).

More than half of the analyses from the drill hole sections through the Middle Ordovician dolomites and limestones were found to be anomalous. These strata are identified in Table 6.2 by blue digits. They lie above the very permeable

Table 6.2

General stratigraphy of the Upper Mississippi Valley District. Data are from Rowan and Goldhaber, 1996. The thicknesses of the principal ore hosts are identified by blue digits and the dominant permeable aquifers by red digits.

System	Series	Formation	Rock Type	Average Thickness, metres
Silurian	Middle	Hopkinton	Dolomite	58+
	Lower	Kamkakee Edgewood	Dolomite Dolomite	10-15 3-35
Ordovician	Upper	Maquoketa	Shale	33-73
		Middle	Galena	Dolomite
	Decrahn		Dol., Lms., Shale	11-12
	Platteville		Lms., Dol.	17-23
	St. Peter	Sandstone	12+	
Lower	Praroe du Chien	Dolomite	0-73	
Cambrian	Upper	Trempealeau	Sandstone	37-48
		Franconia	Sandstone	34-43
		Dresbach	Sandstone	18-43
		Eau Claire	Siltstone, Sandstone	21-101
		Mount Simon	Sandstone	134-238



St. Peter sandstones and below an aquitard, the Maquoketa shale. These anomalous beds are also the dominant hosts of the orebodies in the mining district. The ready interpretation is that a Zn- and Pb-rich hydrothermal solution had flowed through the St. Peter aquifer and the immediately overlying permeable dolomites. The flow interacted with the host rocks and left behind in the basin carbonates with concentrations of hundreds of ppm of Zn and/or Pb but virtually none in the underlying Cambrian and overlying Silurian rocks of the basin. This evidence substantiated the flow path of the hydrodynamic models described above. Next, we have to consider evolving progress on determining (1) the temperatures, (2) duration, and (3) ore component concentrations of the hydrothermal flow along the path through the Illinois Basin and into the ore deposits.

Paragenesis. The precipitation and dissolution sequences shown in relative paragenesis in Figure 6.4 provided many useful clues about the processes that formed these ores.

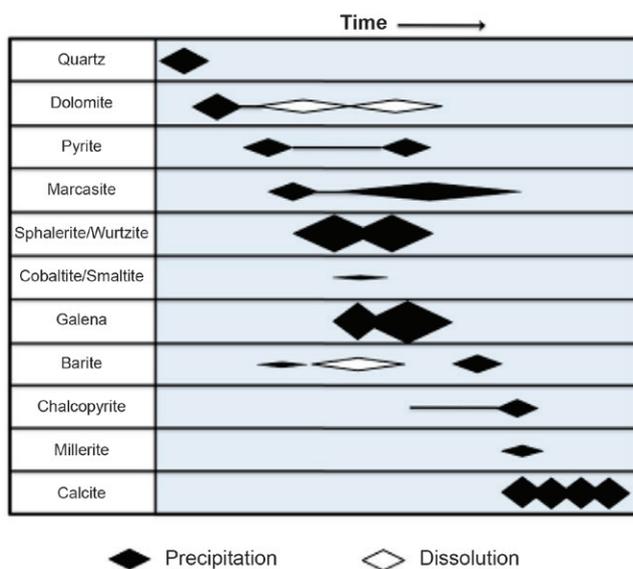
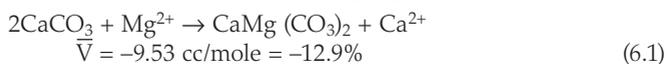


Figure 6.4 Paragenesis of UMVT ores. Prepared by Merce Cobella at Penn State from data in Heyl *et al.* (1959).

The sequences begin with the early dolomitisation of the limestone. That sequence began most likely by the solution adding Mg^{2+} by the reaction:



The molar volume shrinkage that results from this replacement process produced both much open space and often formed local solution brecciation (Fig. 6.5). The results were particular vein structures (often called pitch-and-flat or gash-vein structures) that contained higher sulphide concentrations (Figs. 6.6 and 6.7). Except for dolomitisation, replacement textures are not common in these ores, as explained more recently by Harper and Borrok (2007). These authors have also described a closely related spatial distribution of epithermal dolomite with ore minerals, implying that the same flow produced both sequentially. The space opened by the dolomitisation reaction was partially filled by later minerals including the immediately following iron sulphides. The high proportion of these minerals among the concentrations of ore minerals indicates that the transporting hydrothermal solutions had a much higher Fe^{2+} concentration than of other metals.



Figure 6.5

Solution breccia in the Brunskill West Orebody, Shullsburg, Wisconsin. It is seen best in the incipient structure on the left that becomes more extensive above the pick. These structures are infilled with carbonates, marcasite and sphalerite.

For early barite to be deposited, the incoming ore solution had to carry some Ba^{2+} aqueous species and must have been virtually sulphate-free along the flow path from the Illinois Basin because the solubility product of barite, about 10^{-5} , is so low (Langmuir, 1997). On reaching the ore horizons, sulphate must have been added to the solution either by the oxidation of its H_2S or HS^- contents or, alternatively, by mixing with sulphate in groundwater. However, this second potential source of sulphate is untenable because of the location of the early barite, which is centred within the core of ore mineral zones rather than at their periphery. The prime source of the sulphate requires some *in situ* oxidation of the H_2S or HS^- content and that requires sufficient oxidant from endemic groundwater to form enough sulphate to precipitate the early barite:



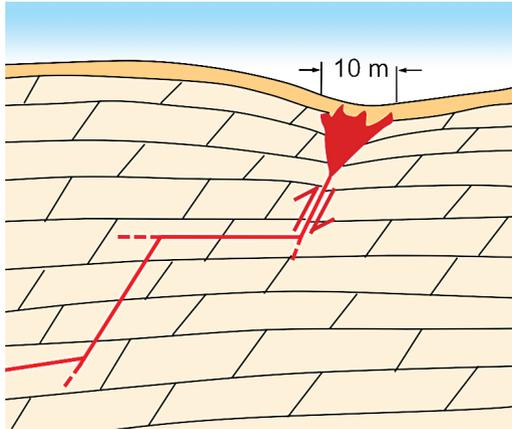


Figure 6.6 Schematic section of pitch and flat fractures, hydrothermally altered and opening upward into a Y-shaped breccia infilled with ore minerals (modified from Barnes, 1983).

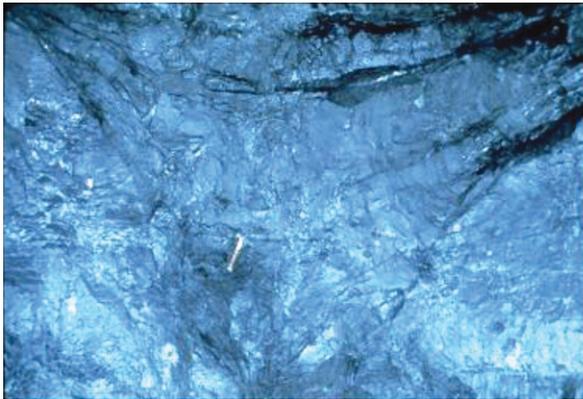


Figure 6.7 A Y-structure 6 m across and filled with slumped solution breccia and sphalerite in a deposit in the East Hayden Mine, Shullsburg, Wisconsin (Barnes, 1983).

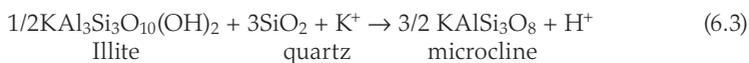
This reaction also releases H^+ , accounting for simultaneous dolomite dissolution where early barite precipitated. Note that air-saturated water at $25^\circ C$ has about 1-8 ppm O_2 depending upon salinity and less at hydrothermal temperatures, so groundwater was a less than abundant source of oxidant to further reaction (6.2). This process deserves new and more complete modelling, such as by starting from data on rates of oxidation by dissolved O_2 from Eary and Shramke (1990).



We knew that oxidation reactions were underway during sulphide deposition because we found a variety of low stability, intermediate state solids, such as FeS_2O_3 , that were captured in pyrite (Kucha and Barnes, 1995). We also showed that the progression from pyrite to marcasite indicated that the pH had dropped simultaneously to 5 or below, for marcasite deposition (Murowchick and Barnes, 1986b). Much of the pyrite had marcasite textures proving that this particular pyrite evolved from ancestral, very common marcasite. Remember that temperatures in the ores, if rising above 160°C , would cause marcasite to recrystallise into pyrite (Murowchick and Barnes, 1986b). For the early barite to be dissolved, later conditions had to become reduced again, probably by continued flow of the virtually sulphate-free primary ore solution. The frequent occurrence of wurtzite in these ores provided another interesting link. *Steve Scott* and I demonstrated that the deposition of wurtzite, rather than sphalerite was linked to the redox state in the primary solution which varied from more reducing – to deposit wurtzite – to less reducing for the more common sphalerite (Scott and Barnes, 1972). Following these ZnS minerals was a later barite stage, signalling that more oxidising conditions became common later in the paragenesis. There again, solution brecciation, apparently due to extra acidity from reactions like (6.2), must have continued as an accompanying process.

The typically euhedral forms of the sulphides suggests that many of the depositional processes were near equilibrium, an inference also indicated by the regularity of sphalerite stratigraphy that we shall see a little further on. The state of saturation conditions clearly changed to far from equilibrium, as seen in polished sections by common corrosion of earlier sulphide layers, especially of sphalerite, that are infilled by later bands (Fig. 6.9c). This textural evidence proves that undersaturation can be extreme enough to reverse the precipitation reactions, although deposition may take place near equilibrium. Hence, precipitation of UMV ore minerals was not a one-way street.

Although silicate alteration is not included in the above paragenetic chart, its distribution is valuable as a means of evaluating the acidity of the penetrating hydrothermal solutions. The veins that provided a path for the ore solution upward into the Y-shaped deposits (Figs. 6.6 and 6.7), had a central sheathing with the assemblage of 2M illite + quartz + microcline. I showed in 1983 that this assemblage was surrounded by later 1 M and Md illites but without microcline (Barnes, 1983). The pertinent stoichiometric reaction is

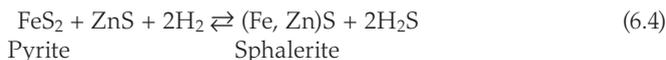


Taking $a_{\text{K}^+} = 0.05 - 0.005$ from inclusion compositions, temperatures of $100 - 200^\circ\text{C}$ and $K_{\text{eq}} \sim 10^{-6}$, the pHs of the primary solutions are about pH 7. We also showed that the common occurrence of microcline in the St. Peter sandstone indicated that this unit carried the ore solution from the Illinois Basin and these results also implied that the primary fluid was weakly alkaline (Giordano and Barnes, 1981). Later during the flow, where the microcline was lost in favour of more illite, the pH had become about 1 unit acidic about where calcite was



dissolved and barite and sulphides precipitated. These three processes document the changes in acidity in the ore zones from initially weakly alkaline to weakly acidic where sulphides were deposited in the pitch and flat and “Y” structures.

Geothermometry and sphalerite stratigraphy. Sphalerite in the UMV ores is banded with colours ranging from opaque brown-black to pale yellow-white. In our lab, Roger McLimans (1977) for his doctoral research determined that the banding is regionally remarkably consistent and has clear implications for the ore-forming process. He measured sphalerite fluid inclusion temperatures and compositions, and $\delta^{34}\text{S}$ in our labs. Figure 6.8 reveals that deposition of the earlier zones A and B began at 75 – 220°C and declined later through zone C. The temperature correction due to pressure variation is estimated to be less than 10°C (Roedder, 1967), and therefore will be ignored because it is similar in magnitude to the uncertainties in the temperature determinations. Zone A is shown in Figure 6.8 together with Figure 6.9 to be comparatively nearly as dark as zone B and much darker than the latest zone C, colours that correlate with FeS contents of 0.3 – 8.5 wt% in zone A, 0.3 – 13.5 % in zone B and 0.15 – 7.1 % in Zone C (McLimans *et al.*, 1980). The distribution of Fe between pyrite and sphalerite among the precipitating sulphides depended also on the oxidation state of the solution during crystallisation:



A strongly reducing solution, with relatively high H_2 pressure and lower H_2S pressure, must have precipitated the darker, FeS-rich sphalerite and less pyrite and vice-versa so variations in the redox state should set the colour of the bands of precipitating sphalerite. For confirmation of his measurements of inclusion temperatures, Roger McLimans compared those with others derived from isotopic fractionation measurements. He found that the temperatures calculated from $\delta^{34}\text{S}$ fractionation between sphalerite and galena were the same as from inclusion data within their combined uncertainties. Perhaps

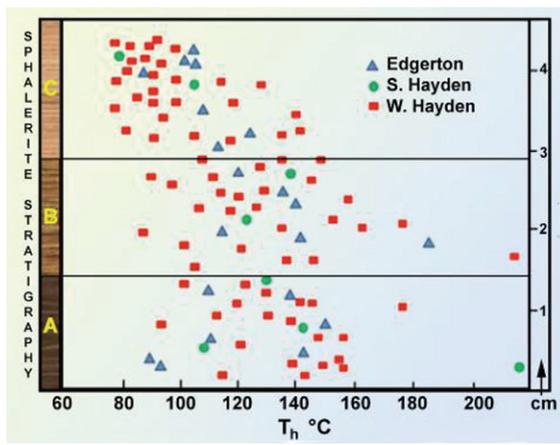


Figure 6.8 Homogenisation temperatures of sphalerite fluid inclusions in zones A, B, and C from three mines in the UMV District (modified from Roger McLimans PhD thesis (McLimans, 1977) and updated through personal communications in 2014).



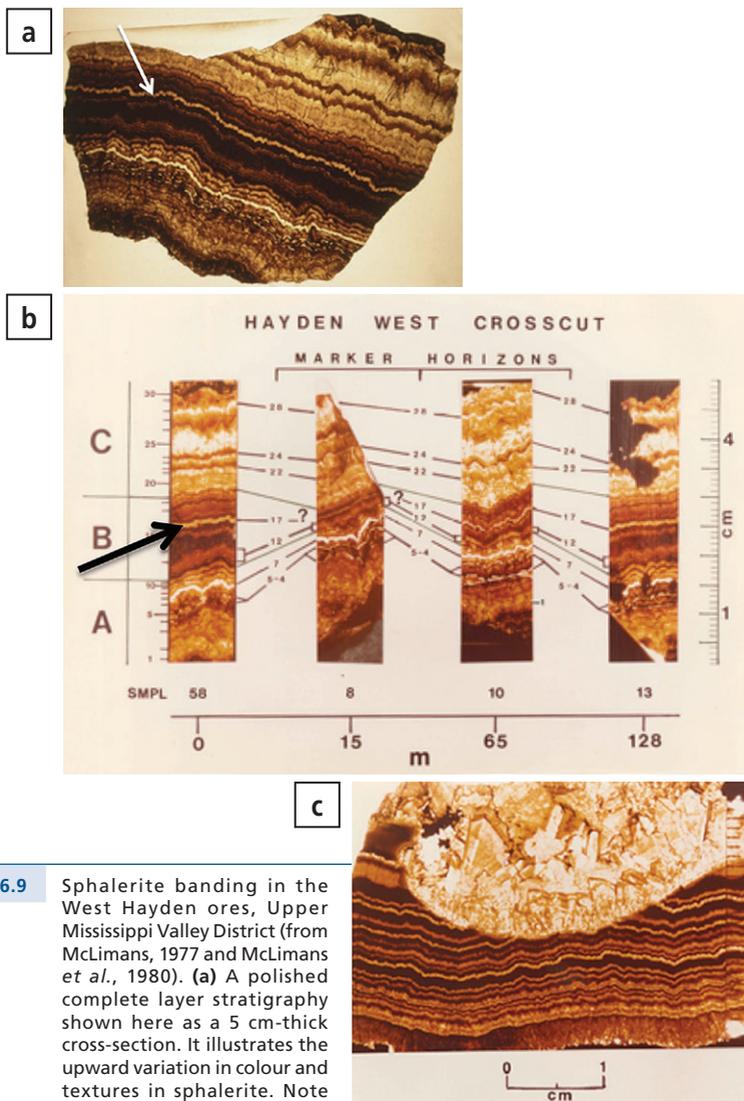


Figure 6.9

Sphalerite banding in the West Hayden ores, Upper Mississippi Valley District (from McLimans, 1977 and McLimans *et al.*, 1980). (a) A polished complete layer stratigraphy shown here as a 5 cm-thick cross-section. It illustrates the upward variation in colour and textures in sphalerite. Note many layers were corroded and later infilled by overlying thin beds. (b) Lateral correlation of the sphalerite “stratigraphy” indicated through thin numbered lines that link across samples (SMPL) from four mineralised zones along a 128 m section in the Hayden West Crosscut Mine; at left shown are the zones A, B and C described in the text and in Fig 6.8. Note the correspondence between these sections; in (b) the middle white band in zone B (black arrow) matches with the wider white band shown in (a) (white arrow). (c) Exceptional corrosion of zones A and B that were later infilled by a more coarse grained zone C.



more interesting is that the sulphide's average $\delta^{34}\text{S}$ of $14.5 \pm 1.5 \text{ ‰}$ is identical with that of middle Palaeozoic seawaters. This similarity implies that the sulphur in the UMV ores of the Illinois Basin could have had a marine source and that the solution had become reduced during its travel through the basin. Inclusions showed no evidence of boiling, even at the highest temperatures of 220°C , so the overburden had to be more than 200 m thick during ore formation. A rough approximation for the depth at the time of mineralisation is about 1 km (Rowan and Goldhaber, 1996).

There have been several investigations of organic maturation in these ores to derive both approximations of temperature and of times of deposition for the UMV District. Although the organic-based temperatures are less precise than those from fluid inclusions, they are in good agreement having a best value near 165°C . Also, a 200 ka duration of the deposition from Rowan and Goldhaber (1996) was based on hopane and sterane ratios. That duration is very similar to our earlier approximation of 250 ka from endogenic organic transport (Gize and Barnes, 1987). The duration had also been established by a very different method

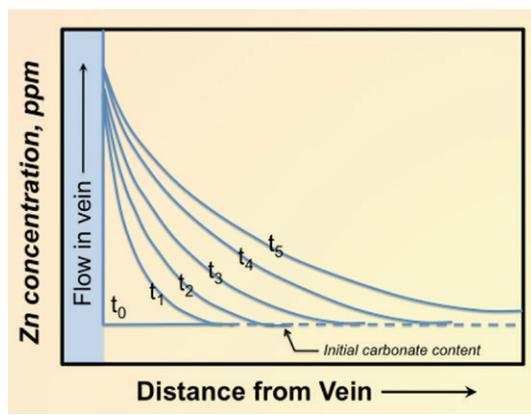


Figure 6.10 The schematic time-dependence of the Zn concentration in wall rocks where controlled by partitioning between the solution and the carbonate host rock and dispersion from hydrothermal flow through a vein (modified from Lavery, 1968).

based on diffusion from mineralising channels into the surrounding host rocks as follows (Lavery and Barnes, 1971).

Therefore, if the diffusion rate were measured experimentally and the solute concentration in the host rocks approximated, then the duration of the mineralisation process could be resolved. For evaluating the diffusion coefficient, a 400 ppm ZnCl_2 solution was presumed. The dispersion process was modelled by the function

$$\frac{\partial(s(\text{Zn}))}{\partial t} = \left(D \frac{\partial^2(s(\text{Zn}))}{\partial x^2} \right) \quad (6.5)$$

Duration of mineralisation. While a hydrothermal solution is flowing through a fracture, its solutes must be diffusing into the wall rocks. A schematic portrayal of this process is shown in Figure 6.10. The longer the flow continues, the broader the dispersion pattern.



where s is the pore surface area/unit volume of host rock, (Zn) is the weight of Zn adsorbed /unit surface area of deposition, D' is the differential diffusion coefficient through the host, t is time, and x is the distance into the host rock (Lavery and Barnes, 1971, equation 11). The match between measured and calculated curves for the major North Gensler, Wisconsin orebody is found in Figure 6.11. A best fit for the time of dispersion is 250 ka from an ore solution with 35 ppm Zn. The same analysis for a comparatively thin 8 cm vein implies a duration of only 2 ka.

There were, in all, four evaluations of the duration of UMV ore- forming process during the last half century, that we can compare for consistency. These are listed in Table 6.3. About $\frac{1}{4}$ Ma appears to be well established as a typical, representative duration. Consequently, the deposition rate for the accumulated sphalerite bands was about $0.2 \mu\text{m/a}$ or 2,500 a per typical 0.5 mm band, neglecting times of corrosion such as those shown by Figure 6.9c. The surprisingly regular bandwidths must be controlled by changes in climate over a few millennia because the deposition rate was only 0.5 mm per 2.5 millennia. The regularity of the banding in the sphalerite stratigraphy (Fig.6.9) implies that the climate was consistent across an area at least as large as this entire mineral district (Mason, 1987). The observed periodicities are implied by single bands at 2,500 a, shown in sections A, B, and C (Fig. 6.9b). these correspond roughly to 80,000 – 90,000 a and 250,000 a for the complete ~3.5 cm section of Fig. 6.9 (b) and the 5 cm section of Fig. 6.9 (a) for the entire ore-forming system.

Our study of the banding of sphalerite is an archetype of the universal three stages of most geochemical research. (1) The conceptional stage when a primary question was proposed and a hypothesis formed: why did such banding occur and what caused it? (2) The second was to identify and collect all of the pertinent data that would best define the nature of the phenomenon. (3) The third stage was to interpret the implications of these data for the geochemistry of the depositional environment and for their general importance to our science. Of course, asking the primary question is easy. However, the second stage, collecting of the data, is typically an arduous, demanding and time-consuming process—the hard work of research. The third stage of digesting the data around a coffee table and the computer can be exhilarating. That is the reward

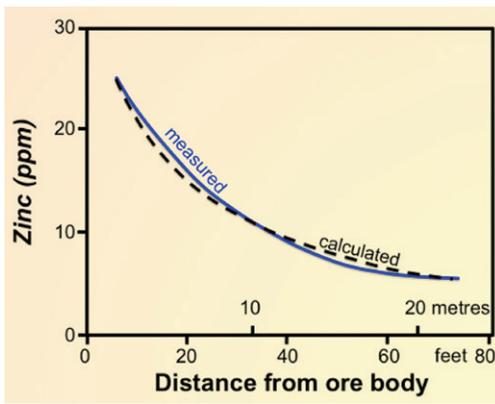


Figure 6.11 Model of zinc dispersion into carbonate host rocks adjacent to the North Gensler orebody, Wisconsin (modified from Lavery and Barnes, 1971).



arising from the study. It is that reward, the discovery that the banding could be correlated over some tens of kilometres, that compensated *Roger* and me intellectually for the many months dedicated to assembling the data and creating an understanding of the problem. To continue this research, our morale was buoyed by a revelation until another climax could be reached generally long afterwards. Optimism was required.

Table 6.3 Timing of sulphide deposition in the UMV District.

Method	Duration, ka	Source
1. Illinois Basin flow modelling	200	Garven <i>et al.</i> , 1993
2. Sphalerite banding	250	Mason, 1987
3. Heat flow modelling	200	Rowan and Goldhaber, 1996
4. Organic maturation	250	Gize and Barnes, 1987

Hydrothermal sources. The modelling of fluid flow through the Illinois Basin has already been discussed. The evidence is conclusive that rainfall onto the southern Appalachians was at a sufficient head to provide the waters that would become hydrothermal during flow through the basin. The salinities in this flow were found by *Roger McLimans* during his PhD research at Penn State (McLimans, 1977), through fluid inclusion analysis, to be at 18-23 wt% NaCl equivalent, about 2/3 saturated. His Cl/Br concentration ratios matched those of seawater at that time, as did also the $\delta^{34}\text{S}$ of the ore sulphides. When considering the very high salinities of the hydrothermal solution, Rowan and Goldhaber (1996) commented that evaporites and shales are rare as potential sources of the high salinities from the Illinois Basin but that palaeo-evaporation could account for the observed concentrations. The inference is that seawater from the Illinois Basin was the source of both the sulphur and the halides of the UMV ore solutions.

At least equally interesting is the source of the metals of these deposits. There had been found, during the last half century reported here, no direct evidence for the sources of the zinc in these ores. In contrast, evidence for lead is more affable. The source of the lead is implicated in a persistent enigma that remained unsolved for many decades. Why are the lead isotopes of the ore galenas anomalously radiogenic-rich with $^{207}\text{Pb}/^{206}\text{Pb}$ at 0.66 – 0.81 (Millen *et al.*, 1995)? *Andy Sicree* offered an explanation and reported it together with more detailed isotopic data measured in *Stan Hart's* lab at MIT on a galena from the South Hayden orebody, Shullsburg, Wisconsin (Sicree *et al.*, 1998). A major clue came from the observation that the most radiogenic leads in the district occurred where the depth between the mineralisation and the Precambrian basement was a minimum (Millen *et al.*, 1995). Also suggestive were analyses finding an average uranium content of 45 ppm for the basement granites (Spirakis and Heyl, 1996), an extreme concentration compared with typical granites at 3-4 ppm U (Rankama and Sahama, 1950).



Single-stage model ages of the basement granites were 1.5 Ga (Van Schmus *et al.*, 1996), much older than the mineralisation found to be at 0.27 Ga (Brannon *et al.*, 1992). The process linking the granite sources to the lead mineralisation is apparent. ^{238}U with a half-life of 4.5 Ga comprises 99.3 % of the uranium content of the underlying granites. It decays via ^{226}Ra , an alkaline earth, with a half-life of 1.6 ka. Being soluble in reduced (low sulphate) hydrothermal solutions, radium was readily mobile in hydrothermal solutions before decaying to produce the exceptionally high ^{206}Pb content of the ores. In our galena analyses, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of the cores of our samples were 0.696 implying that the early hydrothermal solution extracted more Ra from the granites, whereas later flow produced only a ratio of 0.716, a less anomalous level of lead. The relative ^{206}Pb abundances of sampled galenas increased northward across the district which Millen *et al.* (1995) interpreted to mean that the flow pattern was from the south, from the Illinois basin and through the district. A general conclusion is that the source of some of the leads, a radiogenic-rich portion, was from the basement granites along the flow path from the Illinois Basin to the UMV District. That means some flow penetrated below the Palaeozoic section north of the basin and must have combined with the flow through the basin that was documented by the high Zn and Pb trace concentrations of the basin aquifers.

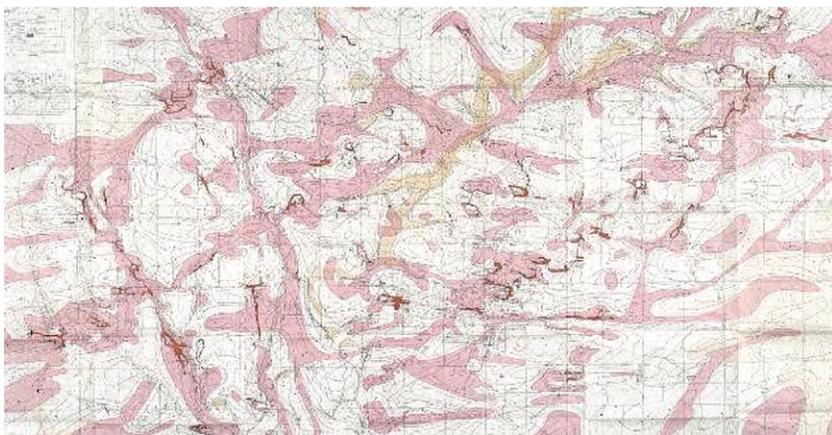


Figure 6.12 Structural geology of the Hazel Green-Shullsburg Area of Wisconsin, 10 × 16 km. The pink areas are synclinal and the red areas are underground mine workings (U.S. Geological Survey Plate 5 from Heyl *et al.*, 1959).

Orebody distribution. The distribution of ore bodies reveals the loci of the causes of precipitation. Figure 6.12 shows that ores are concentrated frequently around the noses of gentle synclines with mostly elliptical shapes, some arcuate, and a few linear (Heyl *et al.*, 1959). Faulting is minor with displacements generally less than 5 m. The sulphides are typically in near-horizontal bodies, most within an elevation range of 15 m and all within a 35 m range. The median dimensions



of 61 ellipsoidal bodies measured by *Mercè Corbella* are 400 m long in an east-west direction, and 150 m wide north-south. The narrow, vertical distribution and the horizontality of the ores indicates that deposition was at an interface between circulating deeper hydrothermal solution and shallower groundwaters in gently warped carbonates (*Arnold et al.*, 1996). That locus is compatible with an environment deduced to be a redox interface, conditions identified by considering of paragenetic data in the earlier section on paragenesis.

Retrospective MVT Evaluations. Hydrothermal research during the last half of the twentieth century was often concentrated on ore mineral solubilities, as examined in detail in Section 3 of this issue of *Geochemical Perspectives*. Several of the labs identified in Table 3.2 completed and published investigations of the solubilities of the principal ore minerals of the MVT deposits, sphalerite and galena. Our lab had contributions on inorganic solubilities of ZnS from *Bill Bourcier* (Bourcier and Barnes, 1987), on PbS from *Tom Giordano* (Giordano and Barnes, 1979, 1981) and on organic complexes from *Andy Sicree* (Sicree and Barnes, 1996). Here, the results from those studies will be used to find how the metals of the UMV deposits might have been carried at concentrations sufficient to deposit ore-level mineralisation.

The dominant MVT metals are listed in Table 6.4. Note that monovalent metals, particularly Cu and Ag, are negligible components. Which complexes could provide the necessary solubilities for the dominant metals very much depends upon the character of the transporting fluids.

Table 6.4 Metals important in the Upper Mississippi Valley District.

Dominant Metals	Minerals	
Iron	Pyrite Marcasite	FeS ₂ FeS ₂
Zinc	Sphalerite Wurtzite	ZnS ZnS
Lead	Galena	PbS
Minor Metals		
Nickel, Cobalt	Millerite Siegenite	NiS (Ni, Co) ₃ S ₄

The nominal conditions commonly accepted, in agreement with the above discussions of the UMV District, are summarised in Table 6.5. They must provide adequate solubilities under near neutral to slightly alkaline, reducing conditions at temperatures up to 220°C or more, with at least 10 ppm of Zn and of Pb (Sicree and Barnes, 1996).

Under such conditions, concentrations in complexes of Cl⁻ and HS⁻ with Pb²⁺ and Zn²⁺ were found to be 10⁻³ – 10⁻⁴x the necessary concentrations for ore genesis, *i.e.* <0.1 ppm, and clearly inadequate for ore genesis (Giordano and



Barnes, 1981; Barnes, 1983; Sicree and Barnes, 1996; Tagirov and Seward, 2010). As summarised by Table 3.3, those are the optimal *inorganic* complexes and they failed as candidates for producing MVT deposits. As alternatives, are there any *organic* complexes that might carry lead and zinc under these conditions, even to 220°C?

Table 6.5 Hydrothermal transporting conditions (Sicree and Barnes, 1996).

Temperature, °C:	125 ± 25 normal, 220 maximum
Depth:	~1 km; equivalent to pressure ~ 250 bars
Acidity:	pH neutral to 1 unit alkaline
Salinity:	18-23 wt% NaCl
Redox:	concentrations: (H ₂ S) >> (SO ₄ ¹⁻)
Σ (sulphide), <i>m</i>	0.01 – 0.001

There have been investigations of organic components present with lead and zinc sulphides under conditions pertinent to UMVT transport. *Andy Gize* found among the sulphides near Shullsberg, Wisconsin considerable quantities of *epigenetic*, low molecular weight hydrocarbons, especially normal alkanes (Gize and Barnes, 1987). However, there was no evidence of important zinc or lead organometallic complexing found in that study although porphyrins could have carried the small amount of nickel present in millerite and siegenite (Table 6.4). In a different approach, *Andy Sicree* tested the transport potential of organic zinc complexing both experimentally (18 different ligands) and with published stability constants (Sicree and Barnes, 1996). Of the types of organic ligands examined, short chain monocarboxylic and dicarboxylate acids and some thiocarboxylic acids failed solubility or stability tests (Giordano, 2002). However, other possibilities, stable under reducing, sulphide-rich conditions, that are yet to be examined in detail include longer chain dicarboxylics (including methyl-succinic, glutaric, and adipic), other thiocarboxylic acids and macromolecular organic compounds (including humic and fulvic acids). Clearly there is much research that must be carried on to further test other organic ligands as potential carriers especially of zinc and lead, and maybe also of iron, nickel and cobalt as well. In the absence of inorganic candidates, further consideration of organic complexing for metal transport into the UMV Deposits is crucial. That is the remaining major enigma in our understanding of the genesis of these ores. During the 50 years of research on these deposits, that was carried out in the latter half of the 20th century, replicate evidence had identified the sources of the hydrothermal fluids and their components, their flow paths, distances and ages, and causes of deposition and its duration, and loci. However, we do not yet understand which solubility-controlling speciation could have produced the MVT ores.



There are apparently two potential sources for the heat that warms hydrothermal ore-depositing solutions. We have seen that for the archetypical Illinois-Iowa-Wisconsin District, the heat was supplied primarily from the depths of the Illinois Basin, by heat flow from the mantle. Evidence for that conclusion is found, for example in the enormous area of uniformly heated deposits and in the absence of igneous intrusions. The characteristics of other MVT Deposits, such as those listed in Table 6.1, are sufficiently similar to the Upper Mississippi Valley District that it is generally accepted that mantle heat flow is the principal engine that powers MVT Deposits worldwide. Several other higher temperature types of deposits are typically spatially associated with intrusives, such as porphyry copper or contact metamorphic types (Barnes, 1997). The proximal intrusives associated with these latter types clearly have provided the second type of heat source, from igneous intrusions. In section 5 of this *Perspectives* I have described the nature of that environment in geothermal systems in the shallow crust about in the top 1 km. Although I could have further expanded on this issue, the characteristics of many of these other higher temperature deposits are far beyond the scope of this *Perspectives*. For their study, I suggest the readers consult the wonderful compilation of articles the third edition of the *Geochemistry of Hydrothermal Ore Deposits* (Barnes, 1997).



The geochemical context that supported hydrothermal research was also maturing rapidly during the last half of the 20th century. Some observations on that progress may improve our perspective on the advances discussed in the preceding sections of this volume.

Both written and verbal communication among geochemists had advanced remarkably since 1950. The expansion of our field required that major changes came about to improve the ease of interaction. Some stages of that progress are historically pertinent both in the written record of general reference volumes and in a revolution in the organisation of our international meetings.

Until about 1950, geochemistry was thought to be a minor subdivision mostly of geology and less of chemistry. The field began to be delineated when collections of data on natural materials were assembled by *F.W. Clarke*, Chief Chemist of the U.S. Geological Survey who published from 1908 to 1924 five editions of “The Data of Geochemistry” (Clarke, 1924). Although there were thousands of analyses and other measurements listed, explanations of the processes that controlled the numbers were missing. It was in 1954 that the volume, “Geochemistry” by *V.M. Goldschmidt* (Goldschmidt, 1954) identified processes that could control the values in *Clarke’s* compilations. That volume announced internationally that geochemistry was a mature discipline in its own right. The first part of *Goldschmidt’s* book explained the principles that controlled atomic distributions and the second summarised the then current information on the geochemistry of each element. This book was published in 1954, seven years after *Goldschmidt* died in 1947, following a long period of poor health beginning about 1917 (Mason, 1992). Some of his writing was done while in hospitals. Friends helped to complete some chapters so that the work could reach fruition. In effect, much of the book was written in the mid-1940s.

Another book also entitled “Geochemistry” by *Kalervo Rankama* and *Th.G. Sahama*, appeared in 1950 with a structure similar to the *Goldschmidt* volume but with much more information on processes and elemental data available after the writing of the *Goldschmidt* book. It was widely accepted as a textbook that further expanded and identified the field of geochemistry (Rankama and Sahama, 1950).

The Geochemical Society began life at about the time that I joined as a Charter Member, 1955. Our Society has been the home for geochemistry during the latter half of the 20th century by providing the dominant meetings, a series of special publications and the leading journal for the field, *Geochemica et Cosmochimica Acta*.

By 1967, there had been such extensive research in the sub-specialty of hydrothermal geochemistry applied to mineral deposits that the need for a summary volume became evident. In response, I assembled chapters by 19 authors into the first edition of the “Geochemistry of Hydrothermal Ore



Deposits" (Barnes, 1967). The vigour of this sub-field was then producing such a remarkable range of advances that they stimulated just about a decade later, the writing of a second volume by 22 chapter authors, some new to the series (Barnes, 1979). Finally, a third edition followed with several changes in subjects and authors, containing 25 chapters and was published just before the end of the 20th century (Barnes, 1997). These three volumes have followed the evolution of hydrothermal geochemistry over three decades.

Important to the development of this field especially was the evolution of geochemical communications during the mid 20th century. First, results of geochemical research were presented most frequently orally at the annual meetings of the Geological Society of America. Geochemical sessions were organised by a program chairman appointed by the Geochemical Society with meeting rooms assigned by the GSA Program Committee. This led to problems as the attendance at geochemical sessions expanded until the seating capacities of the assigned meeting rooms could not accommodate those hoping to hear the presentations. The large overflow caused awkward situations, especially for the geochemical program chairman, a duty I carried out for the 1969 and 1970 GSA annual meetings. By 1983, as Vice-President of the Geochemical Society, I inherited the responsibility to resolve the situation. While flying home from the 1983 GSA Meeting in Indianapolis, *Brian Skinner* (Yale University) and I discussed problems both with room sizes and with geochemical funding. *Brian* proposed that the cure could be found only by creating an annual meeting especially for geochemists. Later when I became the President of the Geochemical Society, I presented that concept in a proposal to the Geochemical Society Council and received an enthusiastic approval. The resulting committee's recommendations to organise an international meeting on geochemistry were also accepted (Barnes and Lasaga, 2004). When *Stan Hart* became the next president, he passed the responsibility for planning the new meetings to me, the past president. The naming of the planned geochemical meetings after Victor Moritz Goldschmidt and events leading to their establishment as a continuing series of meetings are the result. The stimuli for honouring Dr. Goldschmidt are implicit in the 1992 biographic volume "Victor Moritz Goldschmidt: Father of Modern Geochemistry" (Mason, 1992).

The route to the publication of Mason's biography had several twist and turns. Reference materials were largely in German and Norwegian. Initial compilations from them were made by *Denis Shaw*, Professor at McMaster University and long-term editor of *Geochimica et Cosmochimica Acta*. *Denis* simply held the materials for future use. Next, *Charles Sclar*, Professor at Lehigh University, was appointed as chairman of a Geochemical Society committee to advance a centennial celebration of Goldschmidt's birth in 1988, having as a resource *Denis*' collection. The committee persuaded *Gunnar Kullerud*, Professor at Purdue University (and my advisor during four stimulating years at the Geophysical Laboratory of the Carnegie Institution in Washington, D.C.) to undertake writing of the biography. The early compilations from *Denis Shaw* plus the cooperation of the Director of the Geological Survey, of Norway, *Knut Heier*, provided background information but



Gunnar's death in 1989 intervened. The Director immediately asked *Brian Mason*, a staff member of the Smithsonian Institution, to complete the volume. That was especially appropriate because *Brian* had worked with Goldschmidt sporadically from 1940 – 1943 in the Geological Museum in Oslo, Norway.

The biography reveals that for many generations *V.M. Goldschmidt's* Jewish family comprised highly educated professionals, including his father who was professor of chemistry in a series of universities ending at the University of Oslo. Victor grew up in Oslo and received his degrees at the University of Oslo and passed exams in Norwegian, German, Latin, English and French. He received his appointment at Oslo to Professor of Mineralogy in 1914 at the age of 26, remarkably early in the European environment. He had been a docent (~ assistant professor) for only two years. He accepted, from among many invitations, a professorial appointment in 1929 to the University of Göttingen but in 1935 religious persecution caused his resignation and return to the Raw Materials Laboratory of the University of Oslo. However, in 1942 during World War II, he was incarcerated in a concentration camp but escaped to Sweden at the end of the year before being rescued and taken to Scotland in 1943. In spite of failing health, he worked at different institutions in Scotland and gave many invited lectures until, at the conclusion of World War II, he returned home to Norway in 1946 to his Directorship of the Geological Museum and of the Raw Materials Laboratory. Soon, his life ended at age 59 following a cerebral haemorrhage on March 20, 1947.

Goldschmidt recognised the duties of geochemistry to be threefold (Rankama and Sahama, 1950):

- (1) To establish the abundance relationships of elements and nuclides in the Earth.
- (2) To account for the distribution of elements in the geochemical spheres of the Earth, *e.g.*, in the minerals and rocks of the lithosphere and in natural products of various kinds.
- (3) To detect the laws governing the abundance relationships and the distribution of the elements.

The disciplines he applied drew from petrology, both metamorphic and igneous, including treatment of the thermodynamics of phase equilibria, and mineralogy plus crystal chemistry, X-ray spectroscopy, atomic structure, and element radii. He wrote, for example, on the evolution of igneous rocks, on the origin of the earth and the elements and their geochemical classification, and on



Photo courtesy of The Geological Society.

Figure 7.1 Professor V.M. Goldschmidt in 1923.



geochemical cycles. He provided the first tables of elemental abundances in eight monographs, “Geochemische Verteilungsgesetze der Elemente” (Geochemical Distribution of Elements). Demonstrating his versatility, *Victor* opened a new interdisciplinary field by research with a physician to resolve the role of minerals in the development of lung ailments among workers in a glass factory (King *et al.*, 1945).

His research was awarded by memberships in twelve national academies, by three honorary doctorates and honorary memberships in eight scientific societies. *Mason’s* biography (Mason, 1992) in its title identifies Victor Moritz Goldschmidt as the “Father of Geochemistry”.



The Nature of Our Profession

Science is essentially an artistic or philosophical enterprise, carried on for its own sake.

In this, it is more akin to play than to work. But it is a quite sophisticated play in which the scientist views nature as a system of interlocking puzzles. An assumption is that the puzzles have a solution – that they will be fair.

Motivation: fascination with the puzzle itself. Method: a curious interplay between ideas and the compiling of data. The pleasures are those of any artist. High on the list of prerequisites for being a scientist is a quality that defines the rich human being as much as it does the scientist: an ability and desire to reach out with mind and imagination to circumstances outside oneself.

(Modified from an anonymous note found many years ago.)



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GLOSSARY

<i>Ab initio</i>	A calculation based on first, atomic principles.
Activity	A dimensionless thermodynamic pressure or concentration in solids, liquids, gases, or aqueous solutions.
Aqueous	In, or containing, water.
Autoclave	Reaction vessel for experiments at high temperatures and/or pressures.
Bar	A pressure unit equal to 0.1 mega-Pascals or 0.987 atmospheres.
Binary	Compositions between two end member components.
Chronology	The relative times of a sequence of events.
Complex	A bonded set of ions or molecules in a dissolved aqueous species.
Critical pressure	The maximum pressure at the critical temperature above which a compound cannot be condensed to a liquid.
Critical temperature	A temperature above which a compound can exist only in a single (gas) state. At the critical point, the differences in density and composition between liquid and vapour cease to exist and only the vapour persists to higher temperatures regardless of pressure.
Eh	Redox potential for a cell reaction where $E_H = -E_{\text{standard state potential}}^0 + (2.303RT/nF)\log Q_{\text{redox activity ratio}}$
Endogenic	A process originating within the earth.
Epigenetic	Originating after the enclosing host rocks.
Epithermal	A low temperature hydrothermal product.



Equilibrium	A state where forward and reverse processes exactly balance.
Fluid inclusion	A microdrop of fluid enclosed in a mineral solid.
Fugacity	Thermodynamic (ideal) gas pressure in pressure units.
Fumarole	A gas- or vapour-rich volcanic vent.
Geobarometer	An indicator of a rock's formation pressure.
Geothermometer	An indicator of a rock's formation temperature.
Glissade	A slide down a snowy or icy slope.
Hydrothermal	An aqueous, high temperature fluid condition.
In situ	Originating at an item's current site.
Ionisation constant	The equilibrium activity product of the ions comprising an aqueous species.
Ligand	An aqueous species that bonds to other ionic or molecular species.
Magma	A molten igneous rock.
Mantle	The layer of the earth between the crust and the core.
Monte Carlo	A statistical method for unbiased random sampling.
Oxidation	The process of removing electrons from chemical compounds.
Paragenesis	The sequence in which minerals were deposited.
pH	Negative log of the activity of the hydrogen ion in an aqueous solution or $\text{pH} = -\log \text{H}^+_{\text{activity}}$
Phenocryst	A relatively large crystal in a finer matrix of an igneous rock.
Pluton	An igneous intrusive.
Porphyry	An igneous rock containing many disperse large mineral grains (<i>i.e.</i> phenocrysts) dispersed in a finer matrix.
Redox	The oxidation state of an environment where chemical reactions of atoms have their oxidation state changed through gains / losses / transfers of electrons from one species to another.
Replacement	A reaction that converts one or more minerals into a different set of minerals.
Stoichiometry	The elemental composition ratio of a solid or gas or an aqueous species.
Stratigraphy	The sequence of layers of rocks or sediments.
Supercritical	Conditions above the critical temperature and pressure of a fluid.
Thermocouple	A junction of wires with different compositions which generate a temperature-dependent electrical potential.
Thermodynamics	The theory of energy distribution among chemicals.



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DETAILED BIOGRAPHY OF HUBERT L. BARNES

To complement the description of Hu's biography available on the back cover of this *Geochemical Perspectives*, please find below a list of Hu's various honours and achievements.

Hu served on many academic and industrial advisory bodies and to name just a few, he served as the Chairman of the U.S. National Committee for Geochemistry of the N.A.S. National Research Council and was a member of the Governing Board of the American Geologic Institute. Throughout his distinguished career he received innumerable medals, was awarded many fellowships and honorary or guest lectureships / professorships and was the president of various societies and organisations (listed below). This list is far from complete but even so it is a very impressive and well-deserved honours list.

Honours

Fellow, Geophysical Laboratory, Carnegie Institution, Washington, D.C.
Guggenheim Fellow, University of Göttingen, Germany
Senior Humboldt Prize, Humboldt Foundation
Penrose Medal, Society of Economic Geologists
Distinguished Service Award, Geochemical Society
Governing Board, American Geologic Institute
Fellow, Japan Society for the Promotion of Science
Fellow, Geological Society of America
Fellow, Geochemical Society and European Association of Geochemistry



Professorships and Lectureships

Distinguished Professor, Pennsylvania State University
U.S. National Academy of Sciences Exchange Scientist to the U.S.S.R.
Academy of Sciences
Honourary Professorship and Distinguished Visiting Fellow, University of Wales
W.O. Crosby Lectureship, Massachusetts Institute of Technology
Air India Distinguished Professorship, Indian Institute of Technology,
Mumbai, India
N.A.T.O. Guest Professor, University of Nanjing, China
C.F. Davidson Lecturer, University of St. Andrews, Scotland
Royal Australian Chemical Institute Lecturer, Newcastle, Australia
Visiting Professor, Academia Sinica and Ministry of Geology, China
Visiting Professor, Ore Deposits Research Institute, University of the
Witwatersrand, South Africa
Visiting Professor, Mineralogy-Petrology Institute, Heidelberg, Germany
Distinguished Visiting Professor, University of Sydney, Australia
Canadian Institute of Mining and Metallurgy Lecturer
Thayer Lindsey Lecturer for the Society of Economic Geology

President or Chairman

President, Geochemical Society
Chairman, U.S. National Committee for Geochemistry, National Research
Council of the National Academy of Sciences
Co-Chairman, N.A.T.O. Advanced Study Institute on the Geochemistry
of Hydrothermal Ore Deposits, Salamanca, Spain
Chairman, Geochemistry and Mineralogy Program, Pennsylvania State University
Director, Ore Deposits Research Section, Pennsylvania State University
Co-Chairman, National Science Foundation for Geology and Geochemistry
of Gold Deposits, Brazil
Co-Chairman, Second International Symposium, Hydrothermal Reactions,
Pennsylvania State University
Chairman, Goldschmidt Conference, Maryland and Pennsylvania State
University (25th meeting in 2015)

Industrial Appointments

Consulting, 30+ corporations
Four patents
Registered Professional Geologist, Pennsylvania
President, Applied Research and Exploration, Inc., Pennsylvania



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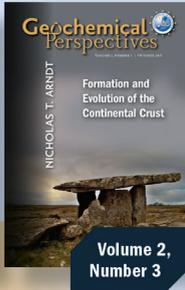
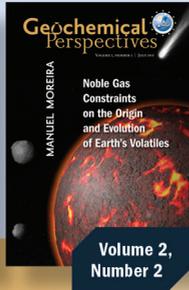
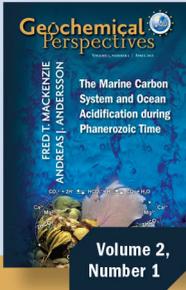
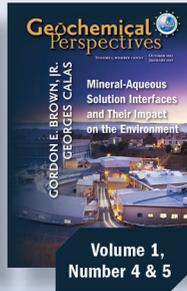
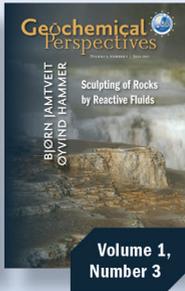
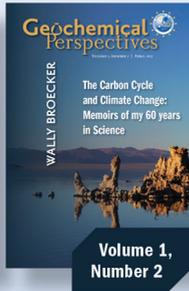
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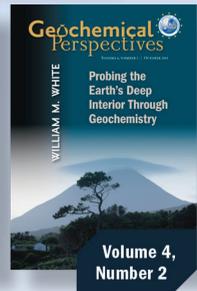
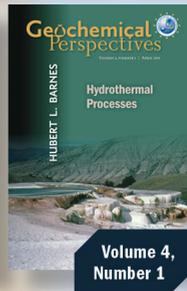
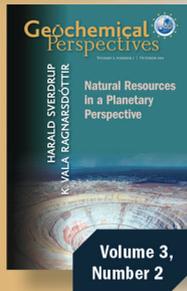
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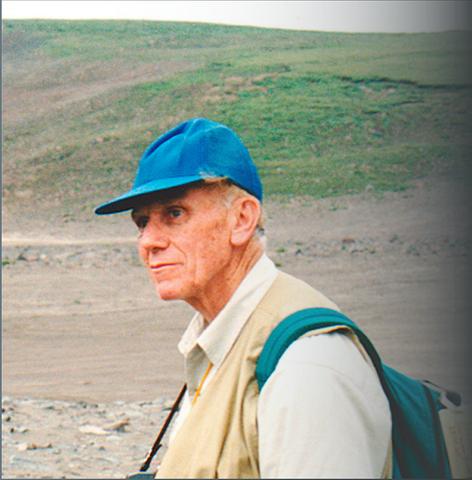


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Taken near the southeast coast of Kamchatka in mid-summer, 1995.



HUBERT L. BARNES is an Emeritus, Distinguished Professor of Geochemistry in the Geosciences Department of the Pennsylvania State University. His research over the last 7 decades has concentrated on hydrothermal processes of geothermal and ore-forming systems. His methods of investigation depended upon both experimental techniques at high pressures and temperatures and thermodynamic and kinetic evaluations. The results were described in about 200 publications and six books that include editing over three decades three volumes that became the principal sources in the «Geochemistry of Hydrothermal Ore Deposits» fittingly termed the G(h)OD books. His scientific career began at M.I.T. as a student and then as a Fellow of the Geophysical Laboratory of the Carnegie Institution in Washington, D.C. Later, he moved to Penn State University as a Professor of Geochemistry and there he also served as Chairman of the Geochemistry and Mineralogy Program and as Director of the Ore Deposits Research Section. His long career included being the President of the Applied Research and Exploration Corporation in Pennsylvania and being a consultant for more than 30 corporations in work that produced four patents. Within the geochemical community, Hu became the President of the Geochemical Society and he was the one who initiated its Goldschmidt Conferences, now the principal annual meeting of geochemistry in the world. The publication of this *Geochemical Perspectives* issue coincides with the 25th anniversary celebration of the Goldschmidt Conference series in 2015 in Prague. A detailed biography of Hu with his many achievements can be found at the end of the issue.