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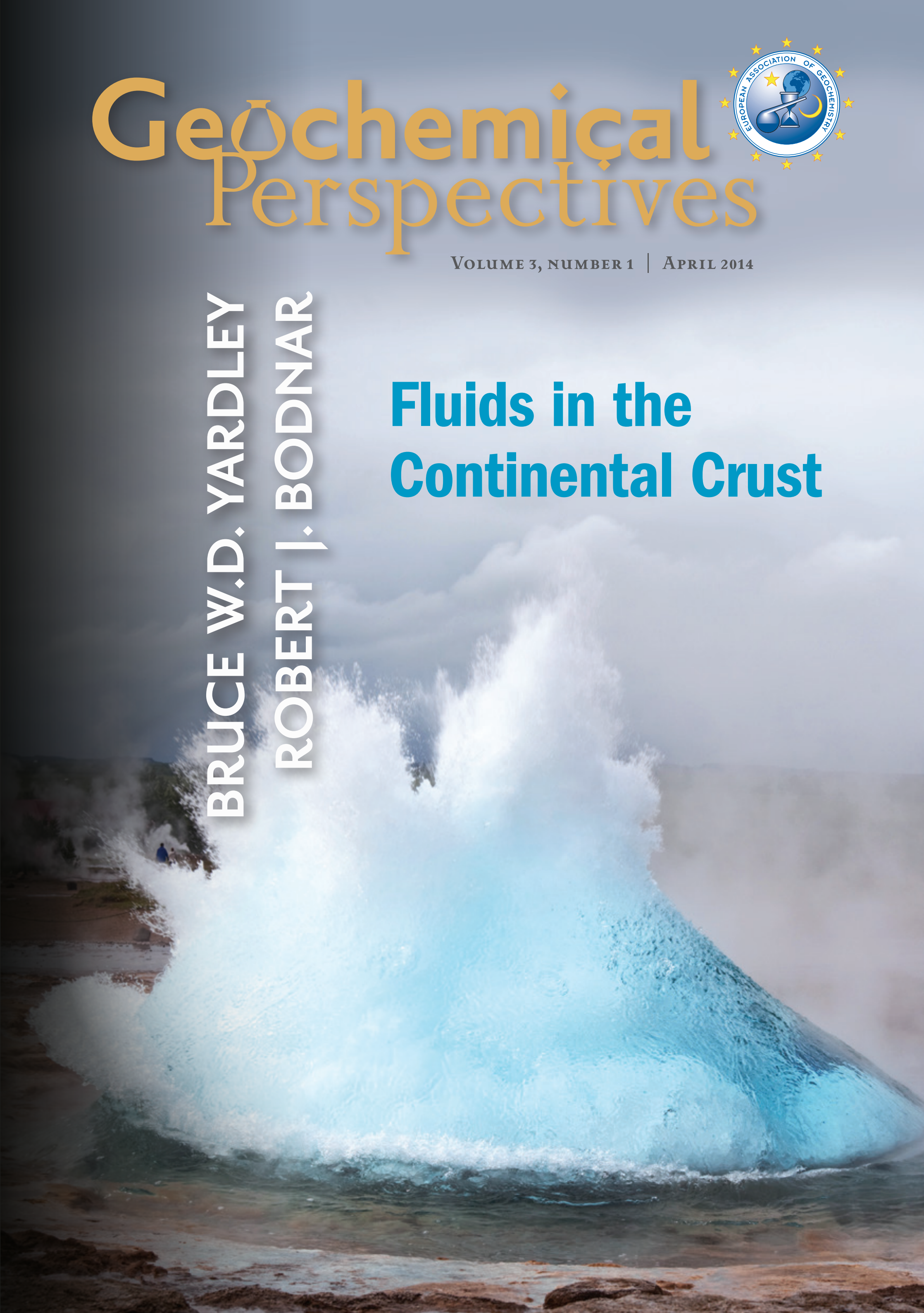
Fluids in the Continental Crust



Geochemical Perspectives

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
The Strokkur Geyser, Iceland. This geyser erupts every 5 to 8 minutes to a height of 30 metres. The boiling of the pressurised water in contact with hot rocks in the subsurface leads to water and steam spraying out of the geyser's surface vent.

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ACKNOWLEDGEMENTS

We would like to thank all of the students and post docs (present and former), as well as co-workers, who have contributed enormously to our understanding of fluid properties and the important role they play in the Earth. This has truly been a group effort and all deserve credit for the advances we have made. We also both thank the many friends and colleagues who have shaped our thinking and changed our ideas over the years.

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FLUIDS IN THE CONTINENTAL CRUST

ABSTRACT

Fluids play a critical role in the geochemical and geodynamical evolution of the crust, and fluid flow is the dominant process associated with mass and energy transport in the crust. In this *Perspectives*, we summarise the occurrence, properties and role that fluids play in crustal processes, as well as how geoscientists' understanding of these various aspects of fluids have evolved during the past century and how this evolution in thinking has influenced our own research careers.

Despite the wide range of possible fluid sources in the crust, fluids in sedimentary, magmatic and metamorphic environments are all approximated by the system H_2O – "gas" – "salt" and normally reflect equilibrium with rocks and melts at the relevant PT conditions. The "gas" component in many environments is dominated by CO_2, but CH_4, as well as various sulphur and nitrogen-rich gases, may also be important. The major "salt" components are usually NaCl and/or $CaCl_2$, but salts of K, Mg and Fe can be major components in specific circumstances. While the activities of many fluid components can often be calculated assuming equilibrium with coexisting minerals, salinity is normally unbuffered and must be determined independently from observations of fluid inclusions.

Solubilities of "gas" and "salt" in H_2O generally rise with increasing temperature and/or pressure, but in many environments compositions are such that phase separation (immiscibility or boiling) leads to the development of salt-rich aqueous fluids coexisting with a volatile-rich phase. Chloride content, buffering assemblages, temperature and, to a lesser extent pressure, all play a role in determining the dissolved load of crustal fluids. In addition to equilibrium considerations, kinetic factors can play an important role in relatively shallow, low temperature environments.

The most important distinction between relatively shallow basinal or geothermal fluids and deeper metamorphic or magmatic ones is the physical behaviour of the fluid(s). In regions where fluid pressure corresponds to hydrostatic pressure, extensive circulation of fluid is possible, driven by thermal or compositional gradients or gravity. In contrast, at greater depths where fluids are overpressured and may approach lithostatic pressure, fluid can only escape irreversibly and so fluxes are generally much more limited.

Much of our understanding of crustal fluids has come from studies of ore-forming systems that are present in different crustal environments. Thus, studies of Mississippi Valley-Type deposits that form in sedimentary basins have shown that the fluids are dominantly high salinity (Na,Ca) brines that have significant metal-carrying capacity. Studies of active continental geothermal systems and their fossil equivalents, the epithermal precious metal deposits, document the importance of boiling or immiscibility as a depositional mechanism in this environment. Ore-forming fluids associated with orogenic gold deposits show many similarities to low salinity metamorphic fluids, consistent with their formation during metamorphism, but similar fluids are also found in some magmatic pegmatites, demonstrating the difficulty in distinguishing characteristics derived from the fluid source from those that simply reflect phase relationships in the H_2O – "gas" - "salt" system. Magmatic fluids associated with silicic epizonal plutons are consistent with experimental and theoretical studies related to volatile solubilities in magmas, as well as the partitioning of volatiles and metals between the melt and exsolving magmatic fluid.

Ore fluids are generally representative of crustal fluids in comparable settings, rather than unusual, metal-rich solutions. During progressive burial and heating of sediments and metamorphic rocks, there is continuous fluid release and loss and the rocks remain wet and weak. Fluid composition evolves continuously as a result of changing conditions. Once rocks begin to cool, fluid is consumed by retrograde reactions and in much of the crust the rocks are effectively dry with a notional water fugacity buffered by the coexisting high-T and retrograde phases. In this case rocks are strong and unreactive.

Our understanding of crustal fluids has advanced by leaps and bounds during the past few decades, and we expect new and exciting results to continue to emerge as new analytical methods are developed that allow us to analyse smaller fluid inclusions in particular, and as theoretical models and experiments advance our understanding of how fluids interact with rocks and minerals in the crust, changing both chemical and physical characteristics.

1. INTRODUCTION

The concept that some form of fluid phase has moved through rocks to create minerals and veins is one that predates modern Earth science and modern definitions of "phase" and "fluid". For example, in the 16th century, *Georgius Agricola* (published in English translation as Agricola, 1912) described "succi" (juices) that lead to the formation of "succi concreti" (solidified juice) – today we know these as veins. Agricola further observed that iron-rust (iron oxides and hydroxides) is formed "when pyrite is softened by moisture", recognising that iron oxides are produced during the weathering of iron sulphides. Over the past century and a half, ideas about crustal fluids and the role of fluids in mass transport and the evolution of the crust have been constantly refined. Sixty years ago, fluids were often invoked as a mystery agent to account for discrepancies between theory and observation – an example is the extensive and now almost entirely forgotten work on "metasomatic granitisation" (see Valley, 2012 for a succinct commentary). Now, our understanding of fluids is much better supported by a combination of observation, theory and experiment. This *Perspectives* article aims to give an overview of those aspects of the compositions and behaviour of crustal fluids with which we are most familiar, and also tells our perspective on the evolution of ideas and opinions about the subject, especially since the 1970's. We largely agree on the ideas and opinions in this article, and where we are writing personally we have tried to make this clear.

The principal observation to emerge from studies of fluid processes across a range of geological environments is that crustal fluids from different geological settings show many similarities. Importantly, the phase behaviour of most crustal fluids can be approximated by the simple H_2O-"salt"-"gas" system, as noted by Kesler (2005) for crustal ore-forming systems (Fig. 1.1). The salt is generally a chloride, and the cation distribution depends on mineralogy, temperature and chlorinity. We will discuss the controls on these variations in Section 2 of this *Perspectives*, but in essence we find that in seawater the dominant cations are Na and Mg, whereas basinal brines are dominated by Na and Ca. Hydrothermal fluids associated with silicic magmatic systems are generally predominantly Na-K fluids, but Fe can sometimes exceed K in these magmatic fluids. Saline fluids associated with more mafic magmas generally contain larger amounts of Ca.

The gas component of crustal fluids is a combination of CO_2, CH_4, H_2S, SO_2 and N_2, and the speciation is dependent on the oxygen fugacity as well as the temperature and pressure (Holloway, 1984). In diagenetic and low-grade metamorphic environments, under reducing conditions, CH_4 dominates and significant H_2S may be present, but at higher grades (higher temperatures) CO_2 becomes more common. In the magmatic environment the gas phase is dominantly CO_2, with the H_2S/SO_2 ratio a function of the oxidation state.

Bowers and Helgeson (1983a,b), Trommsdorf and Skippen (1986) and Skippen and Trommsdorf (1986) were early pioneers in recognising the importance of salts for fluid phase relationships under metamorphic conditions. While it is true that, for example, magmatic and sedimentary fluids differ in the details of their compositions, brines and H_2O-"gas" fluids occur in all crustal settings, and many aspects of their chemistry are independent of their ultimate origin. On the other hand, because those who study sedimentary fluids are often not the same people who study magmatic or metamorphic fluids, work on fluids in these different settings has sometimes focussed on different questions, and we still have much to learn from each other. Those who work on geological samples (rocks, minerals) and those who study active modern fluid-rock systems, similar to the ones that generated these samples, can, and have, learned much from sharing ideas and results. An example we discuss later is the link between epithermal mineral deposits and active, continental geothermal systems. Figure 1.2 is a collection of field photographs illustrating a range of crustal fluid processes, chosen to emphasise this diversity.

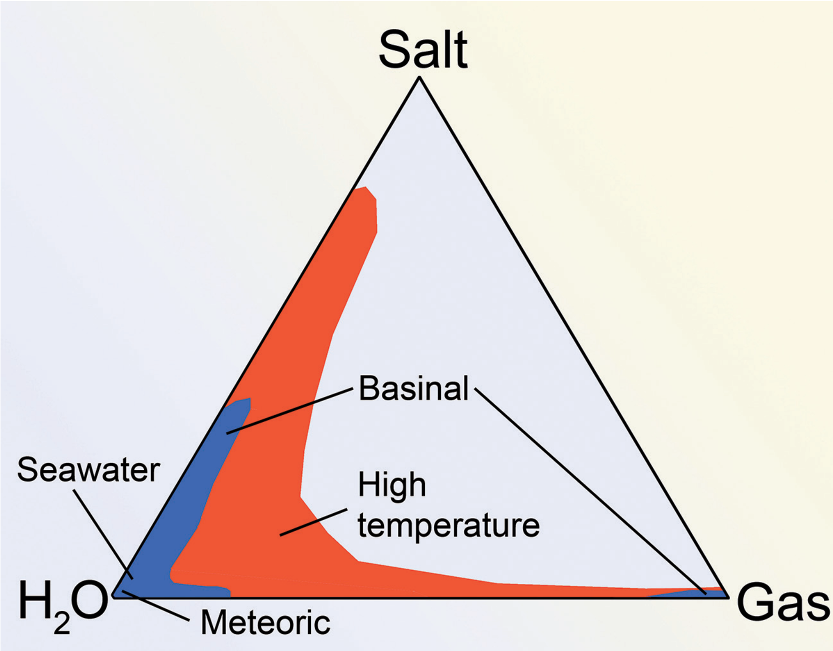


Figure 1.1 Schematic ternary H_2O-"salt"-"gas" diagram showing the possible compositions of fluids in crustal settings at different temperatures (modified from Kesler, 2005). Under crustal conditions, either H_2O-salt or H_2O- CO_2 fluids are possible, with the extent of mutual solubility depending on temperature (and pressure).

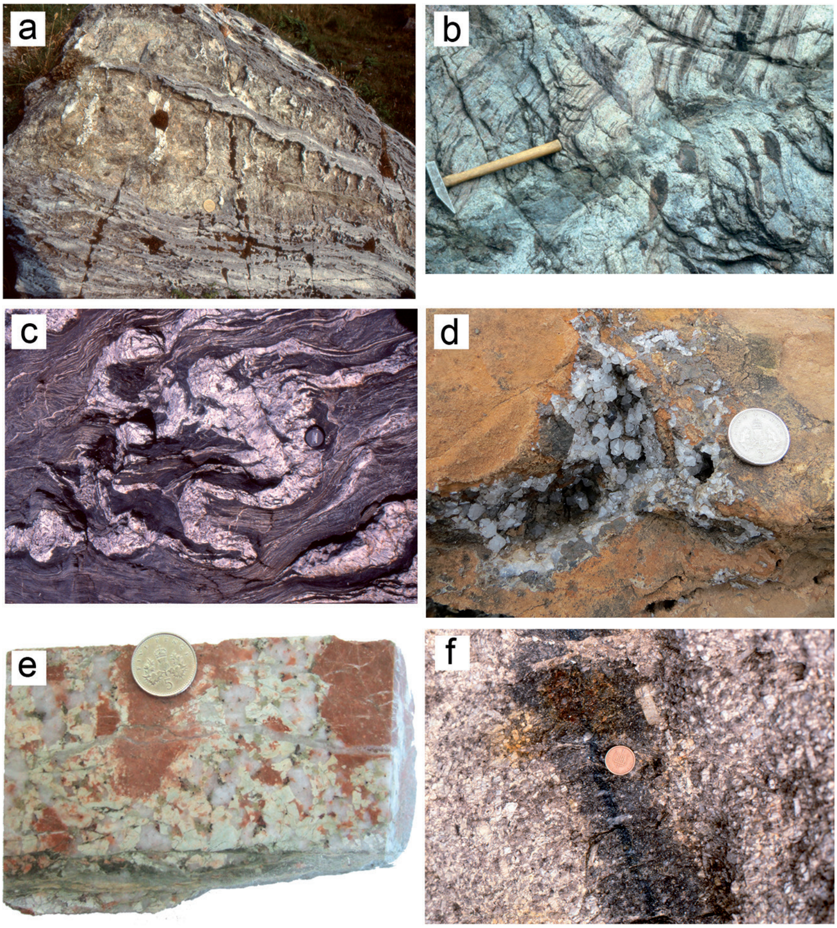


Figure 1.2 Field photographs of a range of rocks modified by crustal fluid processes. **(a)** Coarse grained diopside skarn beds, cut by K-feldspar veins and interbedded with fine grained quartzites. The diopside skarn replaces original dolomite marble bands. Creggs Quarry, Connemara, Ireland. A schematic of the system in which this bedded skarn formed is shown in Figure 3.10. **(b)** Coarse corona gabbro cut by a fine grained shear zone made up of eclogite facies minerals and partially hydrated compared to the original granulite.West Norway. **(c)** Metamorphic segregation veins, predominantly of quartz, in chlorite zone schists. Note the dark zone enriched in chlorite around the intense veining. Lake Hawea, New Zealand. **(d)** Dolomitised Carboniferous limestone containing vein with galena and quartz. Nenthead mine, Cumbria England. **(e)** Example of heavily fractured granite with intensely altered feldspar and veins of quartz and phyllosilicates. Soultz geothermal borehole, nr. Strasbourg, France. **(f)** Greisen in granite. The core of the greisen is a black tourmaline vein and the greisen itself consists of granite within which all feldspar has broken down and been replaced by quartz and muscovite. Cligga Head, Cornwall.

Thermodynamic models span a range of geological settings (and pressure, temperature, composition (PTX) conditions). We are reasonably good at thinking about equilibrium characteristics as a continuum, but while some fluid types, such as brines, occur widely within the crust, others are much more limited in their distribution. For example, fluids that are strongly enriched in elements such as caesium, boron, arsenic, and antimony are mainly known as end-products of extreme magmatic fractionation. The biggest differences in fluid behaviour between different geological settings are probably related to their physical behaviour. In sedimentary basins and shallow crystalline crust, large fluid flows can occur because water is close to hydrostatic equilibrium, effectively connected to the surface, and permeability is relatively high, allowing convection. In deeper hot, ductile rocks, fluids are strongly overpressured and fluid movement is restricted to irreversible leakage. *Note*: throughout this paper we use the term "overpressure" to denote fluid pressures that are greater than the hydrostatic pressure expected at that depth. Fluid movement, and the manner in which fluids interact with rocks, are thus intimately related to the geodynamic and tectonic setting in which the fluids occur. Making connections between the geochemical characteristics of fluids and their involvement in mineral interactions and the hydrogeological constraints on fluid movement is one the most exciting research frontiers for understanding crustal processes. This information, in turn, has important implications for the duration of ore-forming events and the amount of fluid required to create any given deposit.

Bruce Yardley (BY) writes – My fluids perspective developed from an initial interest in metamorphism into a much wider curiosity about the role of fluids in a range of crustal settings. I certainly do not have a comprehensive knowledge of fluids in all possible settings, but I have been lucky enough to have been involved in a number of different approaches to understanding crustal fluids during a time when the field has advanced in leaps and bounds. I first became interested in metamorphic rocks because they seemed very exotic to someone whose home was on the London Clay. As a UK student in the late 60's and early 70's, our view of metamorphic rocks was heavily dominated by structural geology. *John Ramsay* was an enormously influential figure in the UK, and his students had gone forth and multiplied, bringing a quantitative approach to small scale structural geology into geology departments throughout the land. As a result I learned how to recognise and interpret fabrics in regionally metamorphosed rocks long before I understood the subtleties of their mineral assemblages. An enormously valuable training, provided you also add in the petrology.

As I studied metamorphic rocks in the field for my PhD, I became familiar with the veins that they contained. At first, the presence of veins was of interest more as time markers in a history of deformation and metamorphic mineral growth, than as products of fluid processes. In time however, I began to see crustal processes from the perspective of a fluid phase that had a life and a value of its own, rather than perpetually playing Robin to the rock's Batman. My PhD supervisor, *Bernard Leake*, devoted most of his career to the geology of Connemara, a remote, boggy and rain-swept region of the west coast of Ireland; (Ireland was described in the mid 19th century by the then head of the UK Geological Survey as having "the least interesting (geology) of any country with which I am familiar"). After just a few days in the field I reported back to *Bernard* at his encampment – a field with assorted caravans and camper vans where his entire family decamped for the summer – and told him that I had found a pale pink vein mineral which I could not identify. He told me it was andalusite, and he showed me some spectacular examples of andalusite veins nearby. How andalusite forms veins is something I started thinking about then, and still find fascinating.

In the mid-1970's I was a Harkness Fellow at the University of Washington in Seattle when *Bernard Evans* and his students were unravelling mixed volatile equilibria in ultramafic and carbonate rocks and I was able to get a catch-up education in theoretical petrology. *Jacques Touret* came through and enthused us with the joys of studying fluid inclusions, showing me for the first time that you can (sometimes) still see metamorphic fluids. I was also fortunate to meet *Phil Orville* and *Hans Eugster* who had made the fundamental advances in experimental hydrothermal techniques that allowed us to begin to understand fluid-mediated reactions and fluid chemistry. Having a theoretical and experimental framework with which to try to understand metamorphism was an absolute revelation. A few years later, I got a job as a lecturer at the University of East Anglia in the School of Environment, where I got to rub shoulders with geochemists such as *Peter Liss* and *Rob Raiswell*, who actually understood fluids and fluid chemistry from a fluid standpoint. My conversion to combining a fluid view of rocks with a rock view of fluids was completed by working with my graduate student, *Arny Sveinbjornsdottir*, on hydrothermal alteration in Icelandic geothermal systems. Since then, most of my research has attempted to reconcile the sometimes contradictory messages that geologically-based and fluid-based investigations tell us about crustal processes.

Coming from a geology background, it came as a surprise that fluid processes associated with the different classical divisions – igneous, metamorphic and sedimentary, had so much in common. The fluids community took this for granted, as I discovered when I started to attend the Water-Rock Interaction Conferences, but geologists were more compartmentalised. To some extent, this remains the case today; you can still go to meetings and listen to talks by distinguished geochemists who are unaware that in the real world fluids that exsolve from magma contain dissolved salts. For me the key step in breaking down the barriers was the organisation of the first Geofluids Conference in 1993, by *John Parnell* and his colleagues from Queen's University Belfast; shortly afterwards, *Bjørn Jamtveit* took on the organisation of the Kongsberg seminars, and brought together a wonderfully varied group of researchers with interests across the whole spectrum of processes and fluids. A few years later, *Ian Francis*, then working for the publisher Blackwell, recognised the interdisciplinary niche that was opening up and began to discuss with *John Parnell*, *Grant Garven* and myself about the potential for a new journal in the field of geofluids. We agreed there was a need and the journal *Geofluids* was born, the three of us acting as the original

Editors in Chief. The first issue came out in 2001, ensuring that volume numbers and years of publication coincided so that there was one less thing to remember when you wrote out a citation (as you did in those days…).

Robert J. Bodnar (RJB) writes – While *Bruce's* introduction and interest in crustal fluids arose from his studies of metamorphic environments, I came to appreciate the role that fluids play in crustal processes by studying magmatic-hydrothermal ore deposits. My path into the geosciences and to fluids research was tortuous and indirect. As a university student I was both interested in everything and in nothing at the same time. I drifted from one major to another until I was in my final year as a chemistry major at the University of Pittsburgh. Looking for an easy science elective to fulfil my requirements, I took a "rocks for jocks" course and became interested in geology. This was followed by a course on plate tectonics taught by a young and enthusiastic faculty member by the name of *Tom Anderson*. Remember, this was 1974, and the plate tectonic revolution was still in its infancy with many well-known and respected geoscientists as unbelievers. During this course I approached *Tom* and expressed an interest in going to graduate school in geology – something I thought would not be possible for someone with only two geo courses under his belt and a degree in chemistry. *Tom* made a few phone calls, and was eventually able to convince his good friend and colleague at the University of Arizona, *George Davis*, to take me on as an MS grad student. During my first year at the University of Arizona I took all of the courses that would be required of an undergraduate geology major, and began to look around for a thesis project. Being quite ignorant of what the possibilities were for projects, I made my rounds to the various faculty member's offices, introduced myself and said I was looking for a thesis project. Several possibilities were offered, but the one that interested me the most was offered by *Dick Beane* and *Denis Norton*. They proceeded to tell me that they had funding to study the thermal evolution in the lithocap region of a shallow pluton, and asked if I was interested. The clincher was when *Dick Beane* took me to his lab, put a tiny chip of fluorite on the microscope, and instructed me to look at it at high magnification. I looked and I was puzzled. I was looking at a rock – an inanimate object – yet I was seeing hundreds of bubbles dancing around within it. *Dick* went on to explain that these were fluid inclusions and that the bubbles were moving because of Brownian movement, and that the bubbles had been doing so continuously for 10's of millions of years since the fluorite formed. He continued to explain how fluid inclusions form and how they could be used to infer temperatures and compositions of the fluids. Needless to say, the hook was set and I was ready to be reeled in. The clincher came a few months later when *Ed Roedder* visited the University of Arizona as a stop on his Society of Economic Geologists Distinguished Lecturer tour. This was the beginning of a long-lasting personal and professional relationship that lasted until *Ed's* passing in 2006.

1.1 History – The Development of Ideas about Crustal Fluid Compositions and their Effects on Rocks

Interest in crustal fluids was driven for much of the twentieth century by the desire to understand how ore deposits form, and many of the earliest studies of crustal fluids were related to ore deposits. Today however, the importance of fluids for a much broader range of crustal processes, in addition to concentration of minerals in veins, is widely recognised. Water greatly weakens rocks and so plays a major role in determining if and how rocks deform. It enhances diffusion and helps overcome kinetic barriers to reaction, and it lowers the melting points of silicate rocks. Not surprisingly, ideas about the compositions of crustal fluids were initially driven from a lithocentric viewpoint: what mattered was the effect that fluids had on rocks, not the totality of the fluid chemistry or the effect that rocks had on fluid composition. From a thermodynamic approach, this limitation is perfectly reasonable; it is not the composition of the fluid (whether expressed in weight percent or mole percent) that matters but rather the chemical potentials of particular components. The effect of the fluid on the rock and vice versa are both controlled by fluid-rock equilibrium as well as reaction kinetics. But, thermodynamics is independent of the total quantity of fluid and solute, and obtaining an overall understanding of fluid mass transport goes beyond chemical potentials and requires quantities, notably a full chemical analysis. For accessible environments such as sedimentary basins, hot springs, volcanic fumaroles and other relatively near-surface settings, information about the fluids came from direct sampling, but for deeper and/or fossil hydrothermal systems, such as ore deposits, it was necessary to develop an approach based on understanding the way in which rocks change as a result of the introduction of fluids from a remote source, or by studying small samples of the fluids trapped in minerals as fluid inclusions.

Ore deposits are classic examples of open systems, and the key to understanding open system behaviour in thermodynamic terms is encapsulated in the Korzhinskii phase rule, a fundamental law of geochemistry that is still woefully neglected by most modern researchers. *Dmitrii Sergeyevich (D.S.) Korzhinskii* was a truly outstanding scientist who, from the background of *Vernadsky's* pioneering of geochemistry as a whole, developed completely novel and innovative approaches to understand metasomatism in the 1930's. His influence is still present today. Two of his major books have been published in English (Korzhinskii, 1959, 1970). He recognised that conventional chemical thermodynamics, which *V.M. Goldschmidt* had already begun to apply to problems of metamorphic phase equilibria, could be modified to apply to open systems such as ore deposits. In a conventional closed system with 2 degrees of freedom, the number of phases is equal to the number of components, so we can imagine that at any arbitrary P, T condition where a bivariant assemblage is stable, each phase defines the chemical potential of one of the components. For open systems, *Korzhinskii* pointed out that some components have their chemical potentials defined at the fluid source and therefore need not be correlated with a solid phase in the rock. For example, to a very good approximation, seawater penetrating the oceanic crust always has the same composition; as a result it introduces magnesium and sulphate to the crust. In an open system, the number of phases is determined by the number of components derived from the rock's parents (immobile components) – the introduced (perfectly mobile) components do not contribute. This modification of the phase rule successfully predicts that metasomatic rocks should have relatively few phases compared to the number of components present, and that there may well be a decrease in the number of phases in passing from altered wall rocks into a vein. Metasomatic rocks will therefore appear to be high variance assemblages, but any solid solution phases present will show remarkably little variability in their composition. A simple example is the widespread development of quartz veins with talc margins cutting ultramafic slivers in orogenic belts. Only Mg can be considered an immobile component, with Ca removed and Si added by fluid that has equilibrated with surrounding granitic lithologies. As a result the most altered rock is monophase talc, while quartz occupies the fracture space that facilitated the flow.

In addition to developing the theory of open system behaviour, *Korzhinskii* also established the Institute of Experimental Mineralogy in Chernogolovka, near Moscow, where one line of research was the successful replication of metasomatic zoning patterns in the laboratory (Zharikov and Zaraisky, 1991; Zaraisky, 1995).

It was only in the 1950's and 1960's that *Korzhinskii's* ideas were adopted in the West. *Jim Thompson* developed *Korzhinskii's* ideas further, emphasising the importance of local equilibrium for understanding the behaviour of large systems (Thompson 1959). Conversely, Weill and Fyfe (1964) took a purist approach to classical thermodynamics and declared that *Korzhinskii's* modifications of the phase rule were unnecessary. There is a fascinating exchange about the *Korzhinskii* phase rule recorded in the pages of *Geochimica et Cosmochimica Acta* (Weill and Fyfe, 1964; Korzhinskii, 1965; Weill and Fyfe, 1967; Korzhinskii, 1967). Thompson (1970) went on to develop a formalism for open systems, and Rumble (1982) put this in context in a comprehensive overview. For a while, the USA was split from coast to coast by the issue, with Berkeley, California and the *Fyfe* camp rejecting the new ideas from Moscow while Harvard, led by *Thompson*, embraced them fraternally.

A host of important developments in the understanding of crustal fluids date back to the period from the 1950's to 1970's; many of these are described in the classic text of Fyfe *et al.* (1978). Most experimental work during this time focused on either solubility/speciation/mineral equilibria studies or the PVTX properties (Pressure, Volume, Temperature, Composition) of fluids at elevated PT conditions. An important experimental breakthrough was Hans Eugster's development at the Geophysical Laboratory of a way to control (buffer) oxygen fugacity in experiments at elevated P and T (Eugster, 1957). This made it possible to carry out f_{O2} (oxygen fugacity) controlled experiments on Fe-bearing phases such as biotite (Eugster and Wones, 1962) and heralded a remarkable era of experimental innovation, including the experiments by Orville (1963, 1972) on cation exchange between feldspar solid solutions and aqueous fluids. Thanks to the work of *Philip Orville* and *Hans Eugster*, with other pioneers such as *Rosemary*

Vidale, *Julian Hemley* and their collaborators, for the first time we had by the end of the 1960's a measure of what fluids would be like if they were in equilibrium with common rocks in a seawater-like fluid.

Advances in our understanding of crustal fluids during this time also included the efforts of numerous other members of the geochemical community. *Hu Barnes* and his students at Penn State were developing experimental techniques to measure metal sulphide solubilities at carefully controlled conditions. Similarly, pioneering studies of Burnham *et al.* (1969) on PVT properties of pure H_2O, Souririjan and Kennedy (1962) on PTX behaviour of H_2O-NaCl and Takenouchi and Kennedy (1964) and Todheide and Franck (1963) on PTX properties of H_2O-CO_2 at elevated PT conditions allowed us to understand phase behaviour in simple fluid systems at crustal PT conditions. In addition, many studies of fluid PVTX properties were being conducted in the Soviet Union, although this work was not widely known in the West. Other studies focused on determination of the volumetric properties (density or molar volume) of H_2O-NaCl (Hilbert, 1979) and H_2O-NaCl-CO_2 (Gehrig, 1980; Gehrig *et al.*, 1986) at elevated temperature and pressure. A detailed summary of available experimental data on the PVTX and other properties of fluids is provided by Valyashko (2008). These and other studies greatly advanced our understanding of fluid properties at crustal PT conditions, but what we did not know well was what real crustal fluids were actually like. This was about to change.

For both of us, a key breakthrough of the past 40 years, which we think is still under-rated by the wider geochemical community, has been the great expansion of fluid inclusion research, particularly the development of new analytical techniques that allow us to determine major, minor and even trace element abundances in about a half nanogram (10^{-9} g) of fluid. While we have learned much from studies of fluids in active geological environments, such as basinal brines or gases emitted from volcanoes, most of our knowledge of fluid history during ore formation, in particular, comes from studies of fluid inclusions.

The occurrence of fluid inclusions in minerals has been known for at least two millennia. Indeed, *Pliny the Elder* described what were probably fluid inclusions in crystals in his volume "Natural History", written in about 75 AD. In about 400 AD, *Claudius Claudianus* wrote a poem about a large fluid inclusion in a quartz crystal entitled "On a crystal enclosing a drop of water". According to Lemmlein (1950; quoted in Roedder, 1984), the first specific description of fluid inclusions in minerals was by *Abu Raihan al-Biruni* in the 11th century in his book *Kitab al-Jawahir* (Precious Stones). In the 13th century, *Ahmad al-Tifashi* wrote *Azhar al Afkar* (Best Thoughts on the Best of Stones) in which he mentions inclusions ("uyub"), liquid (inclusion) ("ma"), air bubble ("rih"), and mud inclusion ("teen"). Also, at approximately the same time, *Albertus Magnus*, a German scholar and Archbishop of Cologne, wrote a book on lapidary ("de mineralibus") in which he described fluid inclusions in beryl. The earliest known description in English was by Robert Boyle (1672), who described a moving bubble in a quartz crystal. Figure 1.3 provides some examples of the vast range of fluid inclusion types known today from crustal environments.

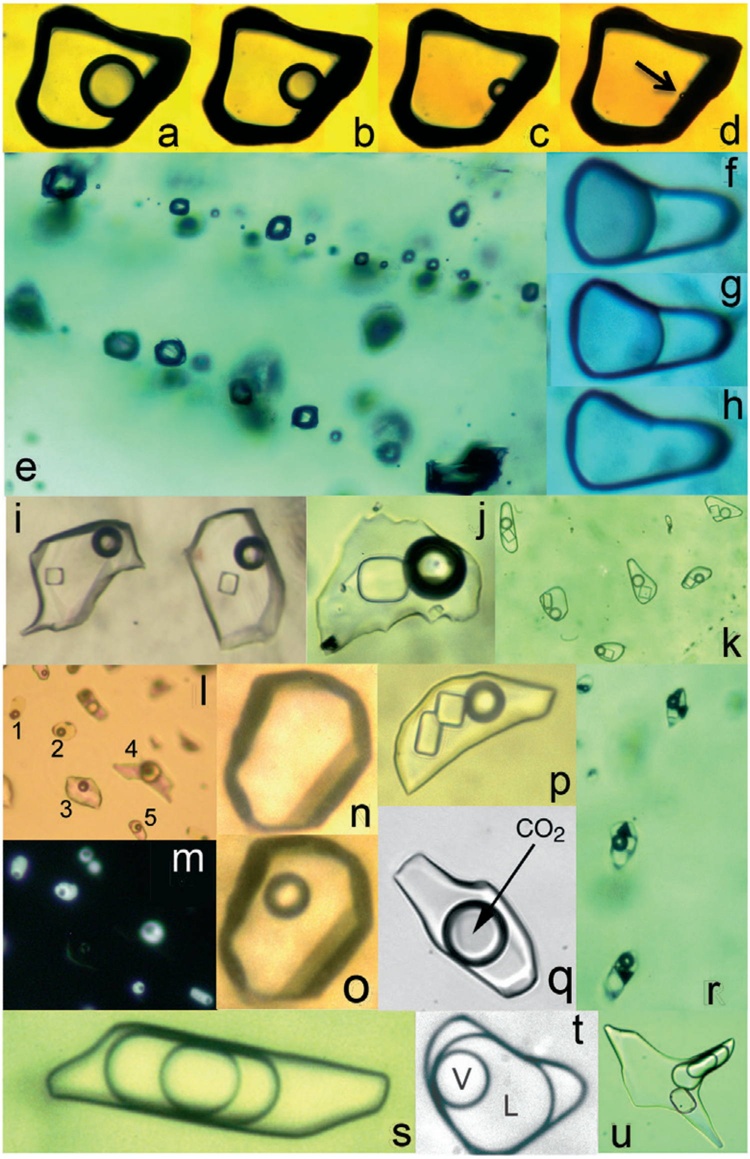


Figure 1.3 Examples of fluid inclusion types from various crustal environments. **(a-d)** Heating sequence for a large two-phase, liquid-rich fluid inclusion in sphalerite from the Creede, Colorado, epithermal Ag-Pb-Zn-Cu deposit. During heating the vapor bubble becomes smaller and disappears at the

homogenisation temperature as the fluid inclusion homogenises to the liquid phase. The arrow in "d" shows the vapor bubble immediately before it disappears. **(e)** Two trails of vapor-rich fluid inclusions in quartz from the Red Mountain, Arizona, porphyry copper deposit. **(f-h)** Vapor-rich fluid inclusion in topaz from the Volnya deposit, Russia. During heating the bubble expands to fill the inclusion at the homogenisation temperature. **(i)** Two halite-bearing fluid inclusions from the Marble Canyon Pegmatite, California. **(j)** Fluid inclusion containing a vapor bubble and several daughter minerals, including a small opaque chalcopyrite crystal. **(k)** Plane of halite-bearing fluid inclusions all containing liquid, vapor, and a halite crystal in uniform volumetric proportions. **(l-m)** Photomicrograph of a group of fluid inclusions in fluorite from the Cave in Rock fluorspar district, Illinois, shown in plane transmitted light (l) and in UV illumination. The entire area of inclusions 1, 2 and 5 (l) is shown to fluoresce under UV light (m), indicating that the inclusions are filled with petroleum. Only the central portion of inclusion 4 fluoresces, indicating that this inclusion contains a droplet of petroleum and an aqueous liquid. Inclusion 3 does not fluoresce, indicating that it contains only brine. **(n-o)** A large inclusion in quartz shown at room temperature (n) and at -90 °C (o). At room temperature the inclusion contains only a single phase, but a vapor bubble nucleates during cooling to -90 °C. This inclusion contains liquid CH_4 at room temperature, and the inclusion has an internal pressure of ~100 MPa. **(p)** Fluid inclusion containing liquid, vapor and both halite and sylvite daughter minerals. **(q)** Two phase fluid inclusion at room temperature containing an aqueous phase and a CO_2-rich vapor bubble. **(r)** Secondary fluid inclusion trail in quartz from the Red Mountain porphyry copper deposit. Each inclusion contains several solid phases, including a large opaque chalcopyrite crystal, indicating that the copper contained in the chalcopyrite was originally dissolved in the trapped fluid, and the chalcopyrite precipitated during cooling to form a daughter mineral. **(s)** Synthetic fluid inclusion containing a CO_2 vapor bubble, liquid CO_2, and liquid H_2O, The composition is 25 mole % CO_2, and this type is characteristic of medium to high grade metamorphic environments. **(t)** Three-phase (CO_2 vapor bubble, liquid CO_2, and liquid H_2O) synthetic fluid inclusion. **(u)** Synthetic fluid inclusion containing a CO_2 vapor bubble, liquid CO_2, an aqueous phase that is saturated in both CO_2 and NaCl, and a halite daughter mineral.

Fluid inclusions were cited as evidence of the hydrothermal origins of ore deposits as early as the mid-19th century by *Ellie de Beaumont*. Soon after, the first systematic studies of fluid inclusions (which he termed fluid-cavities) were made by H.C. Sorby (1858). *Sorby* demonstrated a range of fluid types in rocks and vein minerals, and even proposed methods to obtain information about conditions of mineral growth. He also linked fluids and mineral formation by describing aqueous inclusions in vein quartz, with homogenisation temperatures that decreased outward from an intrusion, a perfect source for ore-forming hydrothermal fluids. In those days, papers published by the Geological Society of London were first presented as lectures in a meeting room designed to be adversarial: friends and opponents of the speaker lined up on opposite sides of the chamber. After *Sorby's* talk, the president of the society at the time apparently commented that it was the least plausible paper he had ever heard presented. This response was not atypical and the subject languished until the mid 20th century, when more sophisticated approaches allowed temperatures of phase transitions to be measured and textural relationships used to separate original inclusions associated with growth of the host mineral from secondary inclusions formed after fracturing at a later stage.

As recently as the middle of the last century, many well-known and respected geoscientists questioned the validity and usefulness of fluid inclusions. Thus, Kennedy (1950b), in discussing the observation that fluid inclusions often indicated a different P-T history than other geothermobarometers, wrote: *"It is our fundamental assumptions in the use of vacuoles [fluid inclusions] in geologic thermometry that need revision".* Similarly, Skinner (1953) reported: *"When evidence from liquid inclusions is at variance with other lines of geologic evidence, as is often the case, it would seem pertinent to consider the possibility that the vacuoles indicate later and different conditions from those operative at the time of formation"*. Certainly this is sometimes true, but such discrepancies are readily recognised by careful petrographic examination following a rigorous protocol that has been developed to test and identify inclusions that have been modified (reequilibrated) (Goldstein and Reynolds, 1994). A turning point in establishing fluid inclusions as a valid and important research tool occurred in 1960 when *Ed Roedder*, *Nikolai Porfir'evich (N.P.) Yermakov* of the USSR, and *Georges Deicha* of France established the Commission on Ore-Forming Fluids in Inclusions of the International Mineralogical Association (COFFI). When this was announced at the International Geological Congress in Denmark that year, there was laughter in the audience; research on fluid inclusions was still considered to be a joke by most of the geologic community (Bodnar, 2007). Soon, however, *Roedder* in the USA, *Lemmlein* and *Kalyuzhnyi* in the Soviet Union, *Deicha* in France and *Dunham* in the UK all helped bring forward and substantiate the validity of fluid inclusions, and by the 1970's fluid inclusion research began to be accepted by the wider Earth sciences community. A whole range of new equipment was developed and applied to a wide range of rock types, and results were integrated with new developments in petrology and geochemical thermodynamics by a wave of new researchers, including *Alain Weisbrod*, *Bernard Poty*, *Jacques Touret* and *Tom Shepherd*. At long last, these and other researchers were providing documentation that the sentiment expressed by H. Clifton Sorby (1858), *"…. that there is no necessary connection between the size of an object and the value of a fact, and that, though the objects I have described [fluid inclusions] are minute, the conclusions to be derived from the facts are great"* was being realised.

For many years, developing the skills to study fluid inclusions and interpret their textures was such a labour of love that fluid inclusionists became a breed apart from most other petrologists, and often their work was not considered in "mainstream" petrological studies. However, as the methods became refined and were explained more clearly, the significance of fluid inclusion studies for geochemistry and petrology at large gradually became established. A series of publications starting with the USGS Professional Paper by Roedder (1972), and including his subsequent review volume (Roedder, 1984), the book by Shepherd *et al.* (1985), short course note volumes including Hollister and Crawford (1981), De Vivo and Frezzotti (1994), Goldstein and Reynolds (1994) and Samson *et* *al.* (2003), and later several excellent websites (*e.g.*, http://fluids.unileoben.ac.at/home.html run by *Ronald Bakker* at Leoben University and the Virginia Tech site run by RJB: http://www.geochem.geos.vt.edu/fluids/), have brought the methods of fluid inclusion studies to a much wider audience. For about 30 years, from 1968 to the mid-1990s, before the days of easy internet access to publications and before most scientific articles came to be published in English, *Ed Roedder* and colleagues *Andrezj Kozlowski* and *Harvey Belkin* compiled abstracts of all publications related to fluid inclusions published each year into a single volume referred to as the COFFI volumes. These also included English translations of many significant articles originally published in Russian, French, Chinese and other languages. This completely volunteer effort led by *Ed Roedder* made it possible for all researchers to access the international fluid inclusion literature and helped to integrate fluid inclusion studies into all sub-disciplines of geosciences. Today, fluid inclusions provide the only reliable source of information about the nature and overall composition of deep crustal fluids, because the concentrations of some key components are not buffered by mineral equilibria. There are enough examples of modern fluid-bearing environments such as sedimentary basins and geothermal fields where both fluid inclusion and bulk fluid samples can and have been analysed, that we can be confident that, with care, fluid inclusions provide an accurate picture of the fluid system at the time of trapping in their host crystal. More recently, starting in the mid-1980s, experimental studies using synthetic fluid inclusions (more details below) cemented the belief that fluid inclusions do indeed trap and preserve a sample of the fluid from which the host mineral grew.

With the widespread availability of reliable microscope-heating-freezing stages in the 1960's, fluid inclusion studies became more than a curious specialisation. In Nancy, France, fluid inclusion research developed rapidly in the 1960's alongside fundamental work on petrological thermodynamics by *Alain Weisbrod* and his colleagues; *Jacques Touret* in particular, realised that fluid inclusion studies could complement theoretical metamorphic petrology, providing information about the fluid to match what could be learned about the solids from electron microprobe analyses. Fluid inclusions are difficult to study in high-grade metamorphic rocks, because all too often inclusions trapped during the prograde event have reequilibrated during retrogression (Sterner and Bodnar, 1989; Vityk and Bodnar, 1995a,b; Bodnar, 2003a,b), and the only inclusions that remain intact are those formed during uplift when retrograde fluids infiltrated along cracks. But they are often readily available in rocks formed at lower metamorphic grades, as well as in magmatic rocks and veins and in shallow geothermal deposits and sedimentary basins. They give an insight into both the nature of the major fluid species present and the dissolved load of the aqueous portion for fluids from a wide range of settings. Simple microscopic observations brought home the message that natural fluids can be very rich in gases, notably CO_2, but also in dissolved chloride salts. *Sorby* had observed this but it was not widely appreciated, though with some notable exceptions. For example, more than a century ago, Lindgren (1905) recognised halite-bearing fluid inclusions at the Morenci, Arizona, porphyry copper deposit and interpreted these as proof that mineralisation was associated with high-salinity fluids, likely of magmatic origin. The existence of ore fluids with such high dissolved loads implied that ore metal concentrations might also be high. Despite this and other reports, the widespread importance of brines in the crust is only now being recognised by a wider community.

The 1978 volume by Fyfe, Price and Thomson "*Fluids in the Earth's Crust*" was a benchmark in the advance of our understanding of crustal fluids, bringing together an enormous variety of research that marked the development of current ideas about crustal fluids and showing how they told a consistent story. Even then, however, the emphasis for ore formation was on the need for strongly focussed flow of large volumes of fluids to produce veins, ores and metasomatic changes. At meetings, *Bill Fyfe* famously talked about the Yangtse River as a unit for fluid volume, and discussed hydrothermal rocks in terms of the number of "Yangtse Rivers" required for them to form. This emphasis reflected a view that even ore fluids would contain only small concentrations of dissolved metals – today we know that this is far from being the case.

The amount of fluid required to form a typical Mississippi Valley-Type (MVT) Pb-Zn deposit provides a dramatic example of how our understanding of the fluid volumes that are required to form ore deposits has evolved over the past half century. Garven (1985) estimated the amount of fluid that would be required to form the Pine Point MVT in Canada, assuming that each kg of fluid precipitated 5 mg (5 ppm) of Zn. Taking reasonable flow rates ranging from 1-5 m/yr, Garven estimated that between 2,500 and 25,000 km^3 of fluid would be required to form the deposits, and the ore forming event would last from 0.5 to 5.0 million years. More recently, Wilkinson *et al.* (2009) analysed fluid inclusions from Irish-type and MVT Pb-Zn deposits by laser ablation ICPMS (Inductively Coupled Plasma Mass Spectrometry) and estimated Zn contents of up to 5,000 ppm in Irish deposits and 3,000 ppm in Northern Arkansas MVT deposits. Using these much higher metal concentrations for the ore-forming fluids, the amount of fluid required to form the Pine Point deposit is reduced to a few 10's of km^3, and it could have formed in a few tens of thousands of years, rather than a few millions of years (Bodnar, 2009). Similarly, recent analyses of fluid inclusions from porphyry copper deposits has revealed copper contents that are 1-2 orders of magnitude higher (summarised in Bodnar *et al.*, 2014) than had been assumed previously, thus requiring much less fluid and/or much shorter times for the mineralising event.

Now that we know that many ore fluids have metal concentrations in the hundreds to thousands of ppm range (we have summarised some of the evidence earlier in Yardley, 2005 and Bodnar *et al.*, 2014), and that rock components may segregate as well as be introduced from an entirely separate source, the fluid fluxes needed to transform rock compositions appear to be much smaller than was once supposed. This example of changing ideas about crustal fluids nicely emphasises another basic point. It is impossible to understand crustal fluid processes from a purely chemical standpoint; it is essential to take into account physical constraints on flow and on fluid availability.

The key to using fluid inclusions to understand fluid chemistry was the development of analytical methods that could be applied to fluid inclusions. Initially, analyses involved crushing tens of grams of pure minerals containing fluid inclusions, leaching the resulting powder with water to extract dissolved salts from the fluid inclusions, and concentrating and analysing the resulting solutions. Early work was summarised by Roedder (1972) and documents remarkable attempts to process large volumes of minerals selected to contain only a single generation of fluid inclusions and no solid impurities whatsoever. With the development of improved analytical methods in the 1970's, the need for large and perfect samples to perform "crush-leach" analyses was diminished. This made it easier to eliminate solid impurities from samples before they were crushed, but even so there were still very few analyses of sufficiently good quality that the charges on the analysed cations came close to balancing those on the anions.

By the end of the 1980s, the combination of much more sensitive analytical instruments, requiring smaller and smaller sample volumes, and the establishment of consistent protocols and procedures (Bottrell *et al.*, 1988) meant that crush-leach analysis was possible using mineral samples of less than 1 g, and could be extended to isotope measurements (Banks *et al.*, 1991), but it still required samples with a single inclusion population.

In the following years, much effort went into developing techniques for chemical analysis of single fluid inclusions -- a holy grail for inclusionists. Although several methods showed promise, it was the concerted effort of *Chris Heinrich*, *Detlef Günther* and their students at ETH Zurich that finally led to a breakthrough (Günther *et al.,* 1998). They combined a short-wavelength excimer laser to give controlled ablation of quartz with an ICP-MS dedicated to laser analysis, resulting in a very low background. Previous attempts had been made with earlier generations of lasers and ICP technology (notably by *Tom Shepherd* and *Andy Rankin* at the British Geological Survey and Imperial College London), but the breakthrough by the Zurich group gave high quality analyses of single inclusions in quartz (the most important and widespread natural host mineral) and was definitive. Of course, many wanted to copy the ETH laboratory, and *Chris* and *Detlef* were wonderfully helpful and welcoming to both of us, who have established laser ablation ICPMS labs based on their design.

A further major innovation of the past 30 years has been the combination of experimental petrology with fluid inclusion studies. The idea is not new: a large part of Sorby's 1858 paper concerns fluid inclusions in synthetic crystals, but with modern hydrothermal apparatus and continued improvements in analytical techniques the approach has finally come to maturity, primarily through the work RJB has led (Sterner and Bodnar, 1984, 1991; Bodnar and Sterner, 1985; Bodnar *et al.*, 1985a; Haynes *et al.*, 1988; Sterner *et al.*, 1988; Vanko *et al.*, 1988; Knight and Bodnar, 1989; Bodnar, 1994, 1995a; Schmidt *et al.*, 1995; Schmidt and Bodnar, 2000; Becker *et al.*, 2008; Lin and Bodnar, 2010).

RJB writes – Much of the experimental work done by my group to study fluids and fluid-melt systems involves the use of synthetic fluid inclusions. The idea to use synthetic fluid inclusions to trap fluids of known composition and at known PT conditions to study fluid properties evolved from a search for standards to test and calibrate a new analytical technique. When I was a student at Penn State, fellow graduate student *Mike Sterner* was working to develop a method to open fluid inclusions with a laser and to analyse the contents by mass spectrometry – this was an early, crude version of the laser ablation ICPMS technique that is used routinely today to analyse fluid and melt inclusions. In discussions over beer (why is it that so many significant advances in the geosciences are made "over beer"?) one afternoon, I recalled a paper I had recently read by Shelton and Orville (1980) in which they described synthetic fluid inclusions trapped by healing fractures in quartz. Importantly, they also noted that the inclusions had densities (homogenisation temperatures) that were consistent with known densities of water at the experimental trapping conditions. So, I suggested to *Mike* that we should try to make synthetic fluid inclusions with known compositions to use as standards. During this time, I was conducting my PhD research in *Wayne Burnham's* lab and *Mike* was working with *Derrill Kerrick*, and between us we had access to a wide range of equipment to conduct experiments at elevated P-T conditions, including cold-seal pressure vessels and internally-heated pressure vessels capable of reaching ~900 °C and ~10 kbar. So, we began to conduct experiments to determine if we could make synthetic fluid inclusions with known compositions that were large enough to be used as calibration standards. We conducted experiments over a range of PT conditions to determine the optimum conditions for inclusion formation, and we tried a wide range of compositions, ranging from reasonable fluids such as H_2O-NaCl and H_2O-CO_2, to ridiculous combinations such as "let's see what happens if we load graphite and sulphur and beer into a capsule!". Needless to say, the results were better than we could ever have expected, and today various modifications of the synthetic fluid inclusion technique that we borrowed from Shelton and Orville are used in labs around the world to study fluid and melt properties at elevated PT conditions. As an aside, when *Mike* and I submitted the first paper describing the technique to *Geochimica et Cosmochimica Acta*, it had the title "Synthetic fluid inclusions in natural quartz. I. Compositional types synthesised and applications to experimental geochemistry." (Sterner and Bodnar, 1984). When Editor *Denis Shaw* returned our reviews, he told us that the manuscript was accepted pending minor changes, but that he was hesitant to let us use the Roman numeral I in the title. He said that too many people submit papers with Roman numeral I to suggest that the paper is the first in a series, but then fail to ever submit another paper in the series. Because we already had a second paper on synthetic fluid inclusions that was in review for *GCA*, *Denis* let us keep the Roman numeral in the title. As of 2014, paper number eighteen (XVIII) has been published, with numbers XIX, XX and XXI in preparation or review. And, of course, the synthetic fluid inclusion technique is now being used in many labs around the globe to study a wide variety of fluid-related processes.

A much more recent major advance in our ability to study fluids experimentally occurred in the early 1990s, when Bassett *et al.* (1993) introduced the Hydrothermal Diamond Anvil Cell (HDAC) for studies of fluids under high temperatures and pressures. The HDAC has been used to extend PVTX properties of fluids to higher temperatures and pressures (Valenti *et al.*, 2012), and the

HDAC has been coupled to a wide variety of analytical instruments to study fluid properties and fluid-rock interactions *in situ*. Schmidt and Rickers (2003) combined the HDAC with synchrotron-X-Ray Fluorescence (XRF) analysis to measure mineral solubilities, and Manning *et al.* (2008) measured rutile solubility in an HDAC mounted onto a synchrotron XRF. An important question for hydrothermal transport is the speciation of metals in hydrothermal fluids and X-ray absorption spectroscopy (XANES and EXAFS) is often used to investigate this. Recently, X-ray absorption spectroscopy has been coupled to an HDAC to study Zr complexation in hydrothermal fluids (Louvel *et al.*, 2013). Wu *et al.* (1995) used the HDAC along with synchrotron XRD to determine the thermal expansion of calcite to 500 °C and 10 kbar. Schmidt and Chou (2012) described the marriage of the HDAC to a Raman microprobe to study fluids at high temperature and pressure. Both Schmidt *et al.* (1998) and Darling and Bassett (2002) used the HDAC as a pressurised fluid inclusion stage to conduct microthermometric analysis of fluid inclusions that generate high internal pressures during heating. One of the limitations of using the HDAC has been the lack of pressure indicators that have sufficient resolution at crustal pressures (up to a few GPa). To address this limitation, Schmidt and Ziemann (2000) calibrated the Raman spectrum of quartz as a pressure sensor for HDAC applications, and Schmidt *et al.* (2013) developed the Raman spectrum of zircon as pressure sensor.

2. CRUSTAL FLUID COMPOSITIONS: THE BASICS

As noted above, crustal fluids are generally composed predominantly of H_2O, with C-species, various salts and variable amounts of rock-forming components. Both nearly pure CO_2 fluids and high salinity brines (Fig. 1.1) occur in some environments. As such, fluids have distinctly lower densities than rocks, and are normally separated from silicate melts (which we will not consider here) by a miscibility gap, as well as by lower viscocities and densities. In the crust, intermediate silicate-rich aqueous fluids only develop in fractionated systems, rich in B and F, where pegmatite melts can evolve. Such fluids can be stable at temperatures as low as 500 ºC at upper crustal pressures (*e.g.,* London, 1986). We note, however, that at PT conditions associated with arc magma generation in subduction environments, there is likely a continuum between water-rich fluids and hydrous silicate melts, without a miscibility gap (Manning, 2004; Kessel *et al.,* 2005; Mibe *et al.,* 2007). For example, in the albite-H_2O system there is complete miscibility at all compositions at T>760 °C at 1.45 GPa (Stalder *et al.*, 2000), and Mibe *et al.* (2007) indicate a second critical end point in the system peridotite-H_2O at about 1,000 °C and 3.8 GPa, corresponding to depths of about 110 km.

Before we delve into the compositions of crustal fluids in detail, it is first necessary to understand their general characteristics and the methods used to study and interpret these fluids. The pressure-volume (density)-temperature-composition (PVTX) properties of fluids represent the most basic information needed to describe the behaviour of fluids at crustal conditions, and usually these are illustrated on phase diagrams with the intensive properties temperature (T) and pressure (P) on the axes. The simplest fluid composition that can be used to model crustal fluid behaviour is the one-component fluid H_2O (Fig. 2.1). In the H_2O system, liquid and vapour may only coexist along the liquid-vapour coexistence curve that extends from its triple point (0.01 °C; 0.0006 MPa; Wagner and Pruß, 1995) to its critical point (373.95 °C; 22.064 MPa; Wagner and Pruß, 1995). At any crustal PT condition that does not lie on the liquid-vapour curve, H_2O exists as a single-phase fluid. In general, when the temperature is less than the critical temperature and the pressure is greater than the pressure on the liquid-vapour curve at that temperature, the fluid is referred to as a liquid. Conversely, if the pressure is less than that of the liquid-vapour curve at that temperature, the fluid is referred to as a vapour. The fluid is referred to as a *supercritical fluid* at all temperatures above the critical temperature. We note that while this terminology is correct for single-component fluids, it leads to confusion for multi-component fluids and we suggest that the term “supercritical fluid” should not be used.

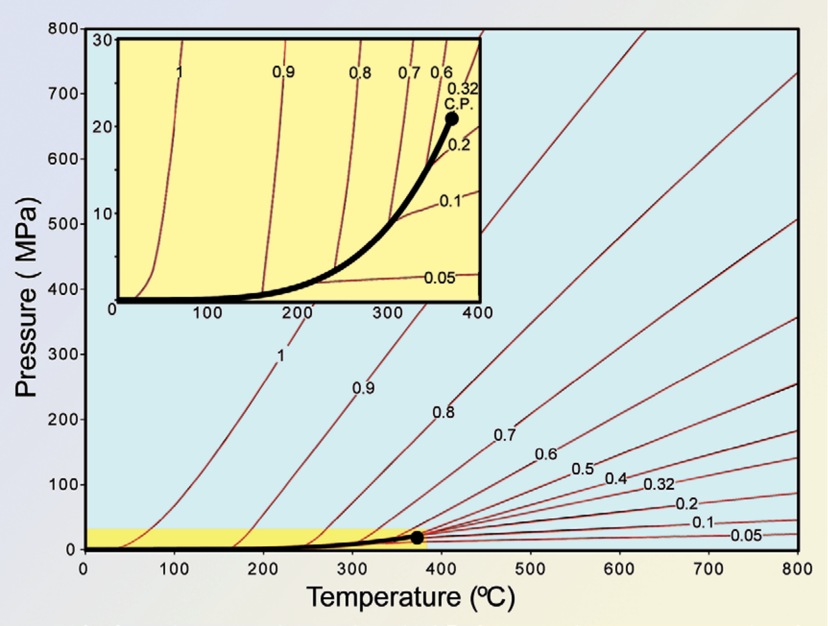


Figure 2.1 PT diagram for H_2O showing liquid-vapour coexistence as a bold curve. The light curves show isochores (conditions where the density of H_2O is constant at the labelled density in g/cm^3) calculated using the IAPWS formulation of Wagner and Pruß (1995).

One of the most important factors that determine a fluid's ability to migrate through the crust is its density, especially the density relative to the surrounding rocks. Moreover, fluid inclusions provide the best method available for estimating the densities of fluids involved in various geological and geochemical processes in the crust because fluid inclusions represent isochoric (constant volume, or constant density) systems. Isochores for H_2O that originate on the liquid-vapour curve and extend to higher pressure are relatively steep, indicating that the fluid (liquid) is relatively incompressible (Fig. 2.1). Conversely, isochores that originate on the liquid-vapour curve and extend into the vapour field are relatively flat, indicating that these fluids (vapours) are highly compressible. The isochore that separates liquid-like fluids from vapour-like fluids is the critical isochore (the critical density is 0.322 g/cm^3; Wagner and Pruß, 1995), which originates at the critical point and extends to higher pressures as temperature increases. From a fluid inclusion perspective, any pure H_2O fluid inclusion with a density greater than the critical density will homogenise to the liquid phase by the shrinking and eventually disappearance of the vapour phase, whereas any fluid inclusion with a density less than the critical density will homogenise to the vapour phase by expansion of the vapour phase to completely fill the inclusion at homogenisation.

The other single-component fluid of relevance to deep crustal fluids is CO_2. Pure or nearly pure CO_2 occurs in sedimentary traps and also in some magmatic and high-grade metamorphic environments, although Lamadrid *et al.* (2014) have recently shown that crustal fluid inclusions that were previously thought to contain pure CO_2 actually contain some small amount of H_2O. While CO_2 fluids are relatively uncommon in the crust, they are conversely quite common in the upper mantle, although even in this environment the fluids contain small amounts of H_2O (Berkesi *et al.*, 2009). Similar to the H_2O system, liquid and vapour CO_2 may only coexist along the liquid-vapour curve that extends from its triple point (-56.558 °C, 0.518 MPa; Span and Wagner, 1996) to its critical point (30.978 °C, 7.3773 MPa; Span and Wagner, 1996). Thus, over the complete range of crustal PT conditions, pure CO_2 will exist as a single-phase supercritical fluid.

Figure 2.1 demonstrates that liquid H_2O is relatively incompressible, because the isochores have relatively steep slopes. As a result, water, if present at the base of the crust, has a density not very far removed from its surface value. In contrast, non-polar fluids such as carbon dioxide (Fig. 2.2) and methane are highly compressible with much flatter isochores.

As noted above, single component fluids are characterised by a critical point that defines the end of the liquid plus vapour coexistence curve, and it is easy to define whether a fluid is a liquid, a vapour, or a supercritical fluid. In nature, fluids are seldom (never?) pure and there are many natural situations in which two fluid phases of different compositions coexist in equilibrium. What should we call the process that produces these two fluid phases, and what do we call the phases?

Traditionally, when two fluids coexist, the denser one is referred to as liquid and the less dense as vapour. This approach works if the densities of the two phases are known and the relative densities remain the same as P and/or T change, but this is not always the case. Thus, in the H_2O-CO_2 system, the H_2O-rich phase is more dense than the CO_2-rich phase at pressures less than about 200 MPa, whereas the CO_2-rich phase is more dense than the H_2O-rich phase at higher pressures. Given this ambiguity, it is more appropriate to refer to the phase by its composition or by its relative density, rather than "liquid" or "vapour". In this *Perspectives* we attempted to use terminology that explains our meaning when it might be otherwise unclear which phase we are referring to. The other point of confusion concerns the process that produces two fluid phases. The term "boiling" is often used to indicate the presence of two immiscible fluids but *sensu stricto* boiling refers to a system in which the composition of the liquid and vapour phases are identical, as for example when liquid H_2O and H_2O vapour (steam) coexist when liquid H_2O is heated to 100 °C at 1 atmosphere pressure (1.01 bar). In multicomponent systems in which the compositions of the liquid and vapour phases are different, the terms effervescence, phase separation or immiscibility should be used to describe the process that produces the two coexisting phases. Here, we use the terms boiling, phase separation and immiscibility interchangeably to describe this process.

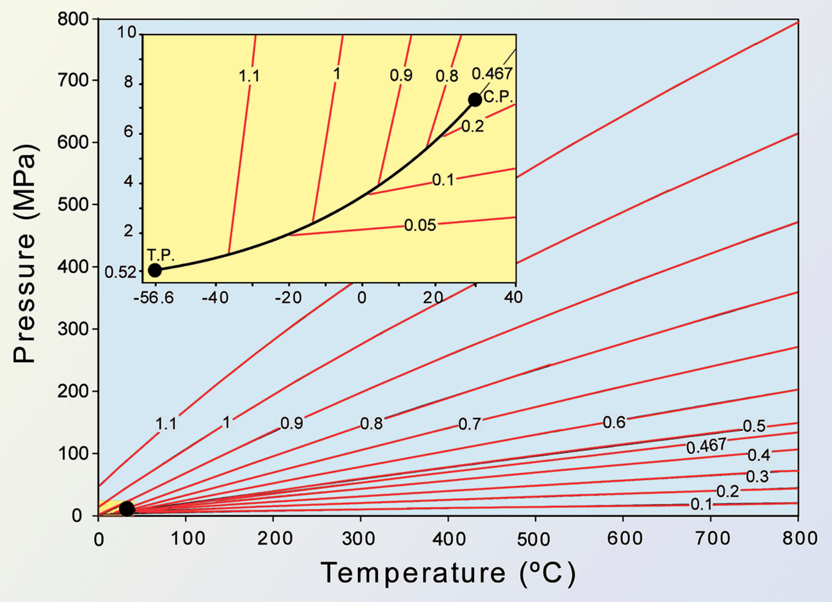


Figure 2.2 PT diagram for CO_2 showing the liquid-vapour coexistence line in bold and isochores of equal density as light curves (density in g/cm^3), calculated using the equation of state of Span and Wagner (1996).

Many sedimentary basins contain highly saline brines, some magmas exsolve brines as they crystallise, and salt melts can be generated from sedimentary evaporite sequences as a result of igneous intrusion (Campbell *et al.,* 1995). The addition of NaCl to H_2O extends the range of liquid plus vapour coexistence (immiscibility) up to pressures of around 200 MPa and temperatures in excess of 3,000 °C (Pitzer and Pabalan, 1986; Fig. 2.3; Bodnar *et al.*, 1985a). Halite solubility in H_2O increases with increasing temperature, although the compositions of salt saturated solutions at different temperatures are only well known to 300 MPa (Becker *et al.*, 2008; Lecumberri-Sanchez *et al.*, 2012). The system H_2O-NaCl (Fig. 2.3) is a good proxy to represent the PVTX properties of saline aqueous fluids in the crust, but we must recognise that other cations, such as Fe, K, and Ca, can be important components of chloride fluids equilibrated with rocks at elevated temperatures (Bodnar *et al.*, 2014). The chemical properties of brines depend very much on the cations that are present. For example, different metal chlorides have different effects on quartz solubility in aqueous solutions (Shmulovich *et al.* 2006).

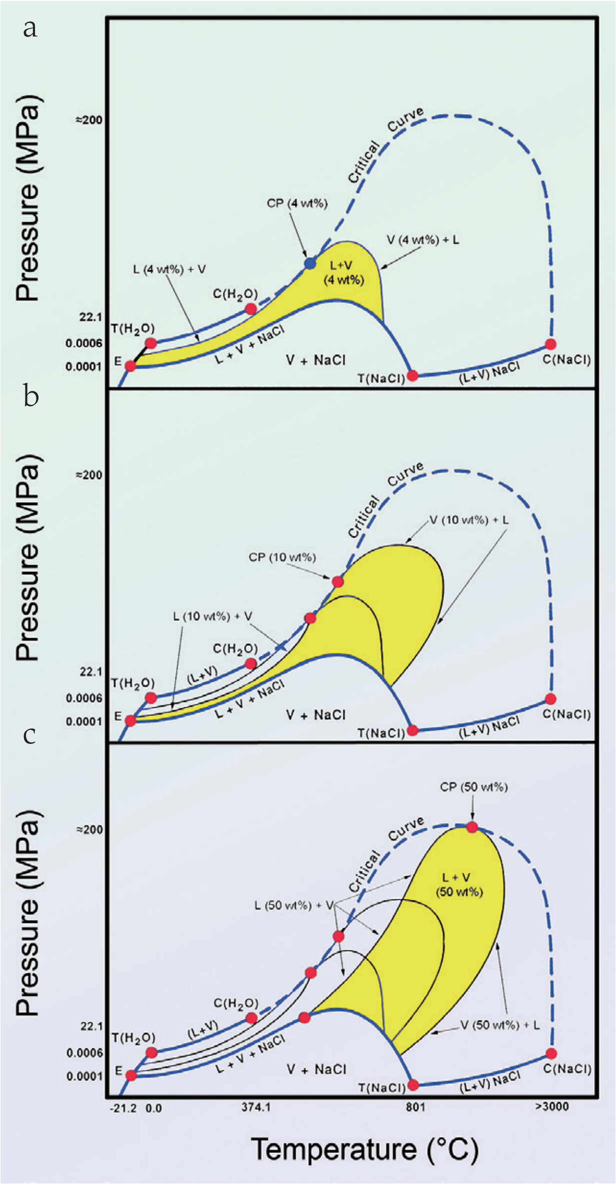


Figure 2.3 PT phase diagram for the system H_2O-NaCl showing the limits of immiscibility for bulk compositions of 4 **(a)**, 10 **(b)** and 50 **(c)** weight percent NaCl. T(H_2O) and C(H_2O) refer to the triple point and critical point, respectively, of H_2O, and

T(NaCl) and C(NaCl) refer to the triple point and critical point, respectively, of NaCl. E represents the eutectic in the H_2O-NaCl system. Lines labelled (L+V) and (L+V) NaCl represent the liquid+vapour coexistence curves for H_2O and for NaCl, respectively. The line labelled L+V+NaCl is the three phase coextence curve where liquid, vapour and halite coexist in equilibrium, and the field labeled V + NaCl is the PT region in which vapour and halite coexist. The dashed line labelled "Critical Curve" represents the locus of critical points in the H_2O-NaCl system that extends from the critical point of H_2O [C(H_2O)] to the critical point of NaCl [C(NaCl)]. CP(4 wt%), CP(10 wt%) and CP(50 wt%) represent the critical points for H_2O-NaCl fluids having compositions of 4, 10, and 50 wt.% NaCl respectively. Fields labelled L+V(4 wt%), L+V(10 wt%) and L+V(50 wt%) represent the PT range over which fluids with bulk compositions of 4, 10 and 50 wt% NaCl respectively, cannot exist as a single-phase fluid and will split into coexisting liquid and vapour phases. Lines labelled L(4 wt%) +V, L(10 wt%) +V and L(50 wt%) +V represent the limb of the two-phase envelope along which a liquid phase of the composition indicated is in equilibrium with a vapour phase whose composition varies along the limb. Similarly, the lines labelled V(4 wt%) +L, V(10 wt%) +L and V(50 wt%) +L represent the limb of the two-phase envelope along which a vapour phase of the composition indicated is in equilibrium with a liquid phase whose composition varies along the limb.

While fluid phase immiscibility can occur over a wide range of crustal PT conditions for H_2O-NaCl fluids, the actual PT range varies as a function of the salinity (Bodnar, 2003c). Thus, relatively low salinity fluids, containing 4 wt.% NaCl, may experience immiscibility at low to moderate temperatures and low pressure (Fig. 2.3a), whereas high salinity brines, containing 50 wt.% NaCl, may undergo immiscibility even at mid-crustal PT conditions (Fig. 2.3c). More typical brines with 10 wt.% NaCl exhibit immiscibility to magmatic temperatures, but only at shallow crustal pressures (Fig. 2.3b).

Saline brines are characteristic of sedimentary basin and silicic magmatic environments, but metamorphic fluids are often (and usually incorrectly) treated by petrologists as binary mixtures of H_2O and CO_2, because of the importance of these species in metamorphic devolatilisation reactions. Greenwood (1962) first demonstrated experimentally the effect that a single phase H_2O-CO_2 fluid can have on metamorphic reactions, as a change in the amount of one component changes the activity of the other. Subsequently, many workers have developed T-XCO_2 diagrams as a way of representing the progress of metamorphism in carbonate-bearing rocks (*e.g.,* Kerrick, 1974). It is implicit in this approach that only a single fluid phase is present.

While H_2O and CO_2 are completely miscible under higher grade metamorphic conditions, this is not the case at temperatures below the greenschist facies where H_2O and CO_2 are commonly immiscible. Unlike the single-component systems H_2O and CO_2, in which two phases (liquid plus vapour) may only coexist for a limited range of PT conditions along their respective liquid-vapour curves, when these two components are mixed, phase separation is possible over a much wider range of PT conditions. The addition of small amounts of

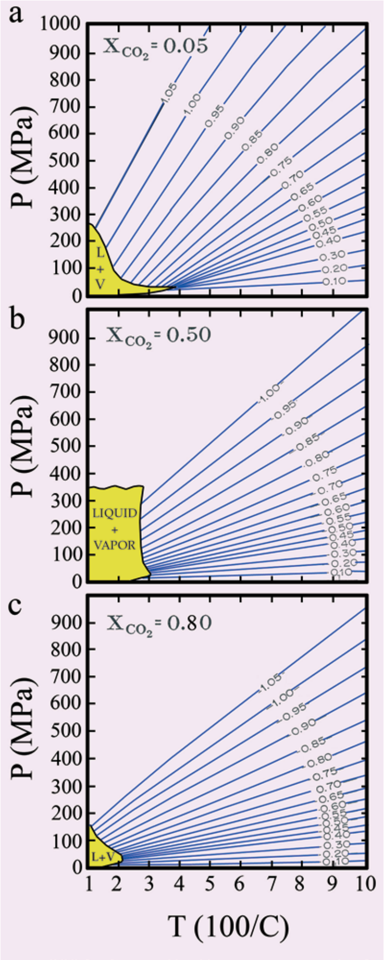


Figure 2.4 PT phase diagram for the system H_2O-CO_2 for compositions of 5 **(a)**, 50 **(b)** and 80 **(c)** mole percent CO_2 (X_{CO2}) calculated from the equation of state of Connolly and Bodnar (1983). The colored region shows the PT region in which a fluid with the composition indicated is not stable, and will split into a more H_2O-rich phase in equilibrium with a more CO_2-rich phase (here labelled L + V).

CO_2 to H_2O results in development of a small field of immiscibility at relatively low temperature and pressure (5 mole % CO_2; Fig. 2.4a). The PT region of immiscibility expands as the proportion of CO_2 increases (50 mole % CO_2; Fig. 2.4b) and then begins to shrink as the pure CO_2 end-member is approached (80 mole % CO_2; Fig. 2.4c). The isochores shown on the series of PT diagrams in Figure 2.4 demonstrate that with increasing CO_2 content, the slopes of the isochores for H_2O – CO_2 fluids become progressively less steep compared to those for pure H_2O, indicating that the fluids are relatively more compressible than pure H_2O.

While the upper temperature limit for immiscibility in the H_2O-CO_2 system is <373.95 °C (*i.e.* the critical temperature of H_2O), or low greenschist grade conditions, metamorphic fluids are unlikely to be composed of pure H_2O and CO_2. Commonly, they contain significant amounts of salts that expand the region of immiscibility compared to H_2O-CO_2 fluids (Bowers and Helgeson, 1983a,b; Skippen and Trommsdorf, 1986; Tromsdorff and Skippen, 1986; Schmidt and Bodnar, 2000; Heinrich, 2007; Liebscher, 2007, 2010; Shmulovich *et al.*, 1995). Figure 2.5 shows the migration of critical points in the H_2O-CO_2-NaCl system, compared to the critical points in the H_2O-NaCl and H_2O-CO_2 binary systems (Schmidt and Bodnar, 2000). These data indicate that natural fluids containing significant amounts of both NaCl and CO_2 may be immiscible over a large portion of crustal P-T conditions.

Compared to the PVTX properties of fluids in the H_2O-NaCl and H_2O-CO_2 binary systems, less experimental data are available for ternary fluids (Takenouchi and Kennedy, 1965). Some ternary phase diagrams, spanning the range from metamorphic to magmatic conditions, are available to interpret the phase equilibrium properties of crustal fluids, and representative diagrams that span a range of crustal PT conditions are shown in Figure 2.6. Data for the densities of multicomponent systems are scarce, with the work by Gehrig (Gehrig, 1980; Gehrig *et al.*, 1986) being the only PVTX data for the ternary system H_2O-CO_2-NaCl that covers a significant region of crustal PTX space. Numerical models, such as those of Duan *et al.* (1995) and others provide an effective framework for predicting PVTX behaviour in PT regions where experimental data are lacking.

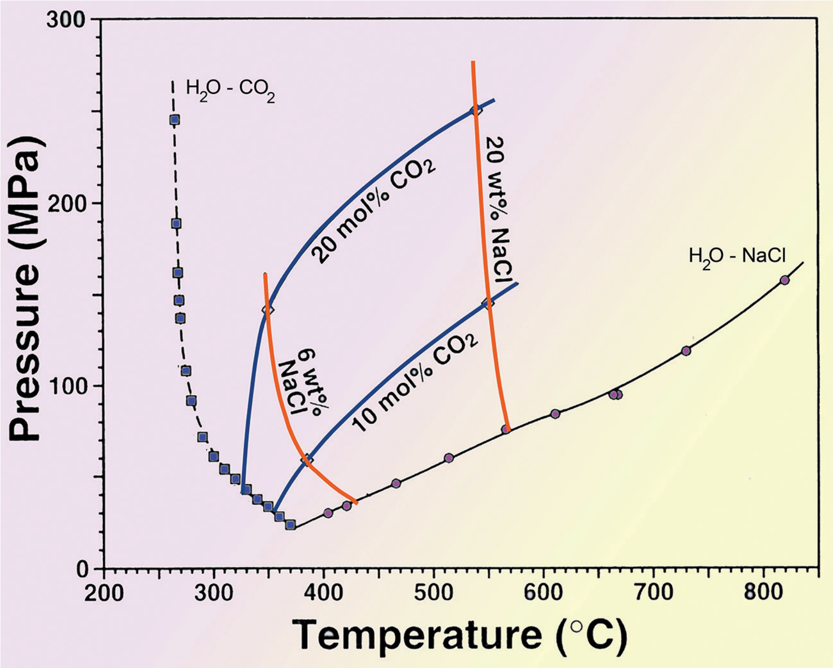


Figure 2.5 PT phase diagram for the system H_2O-CO_2-NaCl showing the critical curves for H_2O-NaCl (from Knight and Bodnar, 1989) and H_2O-CO_2 (from Tödheide and Franck, 1963) and the locus of critical curves for compositions of (H_2O-6 wt.% NaCl)-CO_2 (H_2O-20 wt.% NaCl)-CO_2, (H_2O-10 mole % CO_2)-NaCl and (H_2O-20 mole % CO_2)-NaCl (modified from Schmidt and Bodnar, 2000).

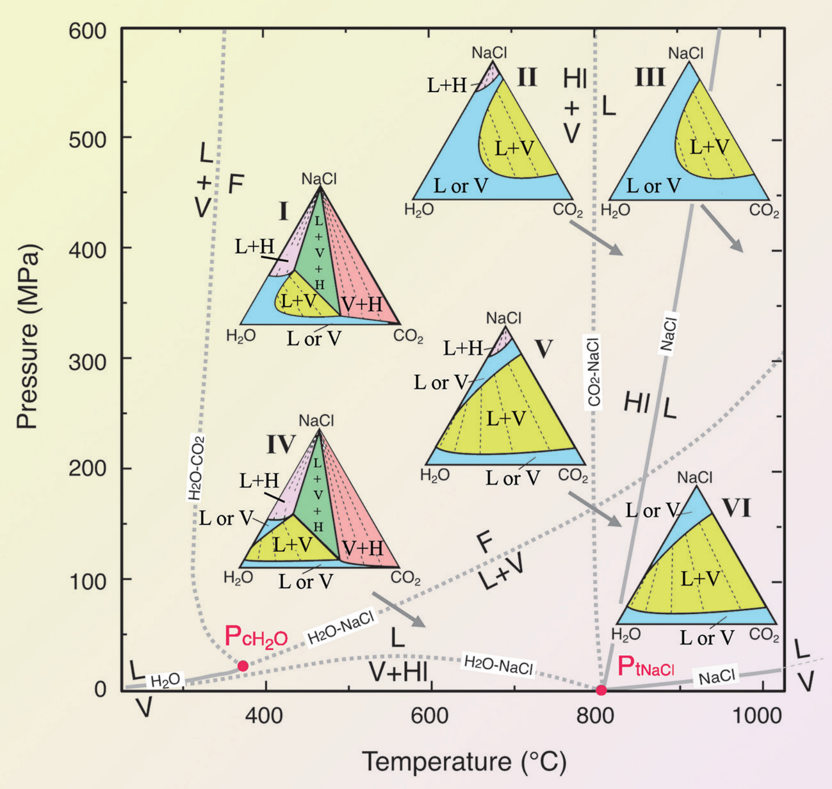


Figure 2.6 Phase equilibria in the ternary system H_2O-CO_2-NaCl at various PT conditions representative of shallow to moderate crustal depths. The seven ternary diagrams show the phases stable in the various PT regions, for various bulk compositions. For example, in region "I", compositions near the H_2O corner and extending to moderate salinity or CO_2 content would be single-phase (liquid or vapour, L or V, depending on the actual PT conditions). More saline compositions along the H_2O-NaCl join would be in the liquid + halite (L+H) field, while compositions along the CO_2-NaCl join would be in the vapour + halite (V+H) field. Intermediate salinity and CO_2-content compositions lie in the liquid + vapour (L+V) field in which liquid and vapour would coexist, with one phase being more CO_2-rich and the other more H_2O-rich. More saline compositions with approximately equal amounts of H_2O and CO_2 lie in the liquid + vapour + halite field (L+V+H). Within each field in which two phases coexist, dashed lines connect the compositions of the two phases that are in equilibrium. With increasing temperature, the liquid + halite (L+H), vapour + halite (V+H) and liquid+vapour+halite (L+V+H) fields become smaller, and only single-phase liquid or vapour, or coexisting liquid+vapour are stable at the highest temperatures shown (modified from Heinrich, 2007).

Why volumetric properties are key to understanding fluids – We noted above that a major motivation for conducting experiments to determine the PVTX properties of fluids at elevated PT conditions is that this information helps us to understand the physical nature of fluids in the crust. However, perhaps more importantly, volumetric (PVTX) properties of fluids are the fundamental data (along with calorimetric data) needed to estimate the thermodynamic properties of fluids. As will be discussed in more detail below, differences in Gibbs free energy represent the "driving force" for chemical reactions and describe how close (or how far from) equilibrium a given reaction has progressed. Assuming that the Gibbs free energy (G) of a system is only a function of the pressure (P), temperature (T) and composition (X), the total differential of Gibbs free energy may be written as:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,X} dP + \left(\frac{\partial G}{\partial T}\right)_{P,X} dT + \left(\frac{\partial G}{\partial X}\right)_{P,T} dX \tag{2.1}$$

or alternatively as:

$$dG = VdP - SdP + \mu dX \tag{2.2}$$

where S and μ represent the entropy and chemical potential, respectively. Comparing the coefficients for dP, dT and dX in equations (2.1) and (2.2) shows that

$$\left(\frac{\partial G}{\partial P}\right)_{T,X} = V \tag{2.3}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_{P,X} = -S \tag{2.4}$$

and, finally

$$\left(\frac{\partial G}{\partial X}\right)_{P,T} = \mu \tag{2.5}$$

The significance of equation (2.2), which is an expression of energy conservation, is that along an isothermal isopleth (a path of constant temperature and composition), the change in the Gibbs free energy as a function of pressure is described by the volume of the system, V.

A simple yet elegant example of the use of volumetric data to determine the thermodynamic properties of a fluid is work of Burnham *et al.* (1969), who determined the Gibbs free energy, enthalpy, entropy and fugacity of H_2O to 1,000 °C and 10,000 bars (1,000 MPa) based on experimental measurements of the density (molar volume) of H_2O. The experimentally determined PVT data were fitted to a ninth-degree polynomial of the form

$$PV = \sum_{j=0}^{9} \sum_{i=0}^{9-j} a_i T^i P^j \tag{2.6}$$

where $a_{i,j}$ represent the fitting coefficients for the polynomial equation. Burnham *et al.* (1969) calculated the Gibbs free energy of H_2O up to 1,000 bars using data for enthalpies and entropies listed in the *Steam Tables* (Bain, 1964). Then, using the PVT data, differences in free energy along isotherms as a function of pressure were calculated from

$$\Delta G = G_P - G_0 = \int_0^P V\, dP \tag{2.7}$$

where subscripts *P* and *0* represent the pressure of interest and standard state pressure (1,000 bar), respectively, and *V* is the experimentally-determined molar volume of H_2O expressed as a function of P at constant T. The Gibbs free energy along isotherms at pressures from 1,000 – 10,000 bars was then obtained from

$$G = G_0 + \Delta G \tag{2.8}$$

where G_0 is the Gibbs free energy at T and 1,000 bars obtained from the Steam Tables (Bain, 1964).

In a similar manner, Burnham *et al.* (1969) determined the entropy of H_2O at 1,000 bars from the Steam Tables and above this pressure calculated the entropy relative to its value at 1,000 bars from

$$\Delta S = \int_0^P \left(\frac{\partial V}{\partial T}\right)_P dP \tag{2.9}$$

The entropy at the temperature of interest and P was then obtained from

$$S = S_0 + \Delta S \tag{2.10}$$

Finally, the enthalpy was determined at 1,000 bars from the Steam Tables, and extrapolated to higher pressures using the previously obtained values for the Gibbs free energy and entropy according to

$$H = G + TS \tag{2.11}$$

where H is the enthalpy. Thus, using the few thermodynamic data available at relatively low pressures, the thermodynamic properties of H_2O were obtained over a wide range of *PT* conditions using only experimentally determined volumetric properties of H_2O. Importantly, this approach takes advantage of the fact that calorimetric methods provide high quality thermodynamic data at relatively low temperatures and pressures, and volumetric data obtained at higher temperatures and pressures may be used to extend the thermodynamic data into the realm of *PT* conditions of interest to geoscientists studying crustal processes. In the extreme case, the thermodynamic properties of a fluid over a wide range of PT conditions could be determined if the thermodynamic properties are known at a single PT point that falls within the range of PT conditions over which volumetric data are available.

Thermodynamic properties may also be estimated directly from PVT data owing to the known relationship between pressure, volume and enthalpy or entropy, at constant temperature and composition, given by (Prausnitz, 1969):

$$dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,X} \right] dP \tag{2.12}$$

$$dS = -\left(\frac{\partial V}{\partial T}\right)_{P,X} dP \tag{2.13}$$

Thus, from measurements of the volumetric properties (density) of a fluid at a known temperature and pressure, the Gibbs free energy, as well as other thermodynamic properties of the fluid, may be calculated assuming that volumetric properties of the fluid may be described by a function (*F*) with P, T and X as independent variables

$$V = F(P,\ T,\ S) \tag{2.14}$$

As noted by Prausnitz (1969), to determine the thermodynamic properties of fluids at some pressure, P, volumetric data must be available not only at this pressure but over the entire pressure range from P_0 to P (or from some pressure where the thermodynamic properties of the fluid are known, perhaps from calorimetric studies).

In a similar manner, the Clausius-Clapeyron equation describes the slope of phase boundaries in PT space, and this in turn may be described as a function of the differences in volume and entropy of the two phases according to:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_a - S_b}{F_a - V_b} \tag{2.15}$$

Thus, experimental studies to determine the PVTX properties of fluids over a wide range of PTX conditions should be of paramount importance in the Earth Sciences, as these data allow us to not only predict and understand fluid behaviour in the crust, but also provide the basic information needed to develop a rigorous thermodynamic framework in which to interpret fluid-mediated processes. A classic example of the application of this approach was described by Burnham and Davis (1971, 1974), who measured the PVTX properties of the system alibite-H_2O and then applied the methods described above to determine the thermodynamic properties of this system over a wide range of PTX conditions.

Because the thermodynamic properties of fluids may be calculated directly from the PVT properties of the fluids, we would expect that relative changes in the volumetric properties should scale with other thermodynamic properties, and this is indeed the case. In particular, in the vicinity of the critical point of H_2O and along the critical isochore, the density (or molar volume) of H_2O changes by a large amount with small variations in either pressure or temperature. Johnson and Norton (1991) defined this region of PT space the "critical wedge" and reported that the ability of fluid to transport mass and energy in this region is very sensitive to temperature and/or pressure fluctuations. Thus, many thermodynamic and transport properties of fluids that are described by partial derivatives involving pressure, temperature or volume, including isothermal compressibility (β), isobaric expansivity (α), isobaric heat capacity (C_P), and many others diverge towards $+/-\infty$ at the critical point. Johnson and Norton (1991) further note that the PT region in which aqueous fluids exhibit this anomalous behaviour (~350 to 450 °C and $\sim 200 < P < 1{,}000$ bars) corresponds to PT conditions that are common in many shallow crustal hydrothermal systems. More recent work (Klyukin *et al.*, 2014) shows that this region of enhanced transport properties migrates in concert with the critical point to higher PT conditions as salt is added to the system.

In terms of their potential for mass transfer, discussed more extensively below, CO_2-poor NaCl-H_2O fluids (those that lie along the left hand side of the triangles in Figs. 1.1 and 2.6) clearly have considerable potential to transfer a wide range of metals as chloride complexes. In contrast, NaCl-poor fluids lying along the base of the triangles are generally richer in soluble gases and in those metals whose solubility is enhanced by dissolution of gases. The existence of these two classes of fluid is ultimately dictated by fluid phase equilibria, not the geological source of the fluids.

The presence of a second fluid phase also has a profound effect on mineral phase relations and metamorphic equilibria because it reduces the number of degrees of freedom in the system (Bowers and Helgeson, 1983a,b; Skippen and Trommsdorf, 1986; Trommsdorf and Skippen, 1986), while also ensuring that the composition of fluid entering or leaving a system does not have to be the same as the average bulk fluid composition at the time (Yardley and Bottrell, 1988).

The separation of a single H_2O-NaCl-CO_2 fluid into a more dense phase containing most of the salt and a less dense, volatile-rich phase has an enormous impact on mineral solubility and mass transfer, as we can judge very simply from the formation of calcium carbonate scale in a domestic kettle as the water boils. Flow rates of fluids of different densities and viscosities are different, and the consequences of their mixing when fractures or cavities open and draw in all fluids from surrounding rocks provide enormous potential for ore formation. A wide range of disparate ore deposit types, including epithermal precious metal deposits, porphyry copper deposits, and orogenic gold deposits, share as a common characteristic a link between ore formation and fluid immiscibility.

In this *Perspectives*, we include only fluids occurring as a free phase (or phases) in the crust, *i.e.* excluding the role of fluid species present in mineral lattices, defects, inclusions or on grain boundaries in otherwise fluid-absent rocks. In the deep crust and upper mantle, most H_2O occurs within hydrous phases or dissolved in melts rather than as a free fluid phase, whereas deeper in the mantle most H_2O (and probably most CO_2) is contained within the structure of nominally anhydrous (volatile-free) minerals (Bodnar *et al.*, 2013a). While it is certainly true that water in defects or adsorbed on grain boundaries has an important impact on how minerals behave relative to a truly anhydrous reference, the difference between fluid-present and fluid-absent processes is the first order distinction in the crust. An aqueous fluid is the prerequisite for mineral dissolution and growth (as succinctly demonstrated by Putnis and Austrheim, 2010) and only where there is fluid can there be pressure solution, the most effective deformation mechanism under most crustal conditions (Rutter, 1983). As well as defining differences in chemical potentials, fluid availability has a fundamental impact on transport processes and the extent to which fluid-moderated processes can take place. Diffusion through a static pore fluid is much more effective than diffusion through minerals, or indeed through grain boundaries, while much greater mass transport will take place if a fluid charged with solutes is sufficiently abundant such that it can migrate through the permeability structure of a rock.

Having established the general compositions of fluids that occur in the crust, most geochemists are then keen to know more about the chemical nature of the dissolved load of the fluid. Over the past half century our understanding of crustal fluid chemistry has advanced in two parallel directions. One is an approach based in chemistry, working from first principles to define, for example, species activities in solutions that are saturated with respect to particular minerals and epitomised in the classic text by Garrells and Christ (1965). The other involves direct studies of natural fluids, and these have defined the range of chemistry that is important for understanding crustal fluids and their effects. The two approaches are complementary: it is fundamentally impossible to predict the dissolved load of a fluid without knowing its chloride content (*cf.*, Holland, 1972), and this is an element that is not normally buffered by mineral chemistry but can be quickly estimated from fluid inclusion studies. At a more pragmatic level, we cannot yet model activity composition relationships of very concentrated solutions under extreme conditions, but there are now many good analyses of such fluids for a wide range of components.

We can think of the solute load of crustal fluids as comprising two parts: aqueous electrolytes and volatiles, and "rock components", *i.e.* Si and Al. The relative concentrations of various electrolytes can vary by cation exchange with the surrounding rock, but the total concentration of dissolved cations must maintain a balance with the anion load. In contrast, Si is best thought of as forming neutral complexes in solution (nominally H_4SiO_4), so that the dissolved load of Si largely reflects temperature and pressure (except at extreme pH); usually crustal fluids can be assumed to be at quartz saturation. Over most crustal conditions, the dominant dissolved load in aqueous fluids consists of electrolytes, which are dominated by chloride salts. Their behaviour is dominated by the dielectric properties of water, which are closely related to density. Thus, from the PVT properties of H_2O (Fig. 2.1), we can expect metamorphic fluids at high pressures and temperatures to be dominated by dissociated species, much as at surface conditions, while at near-magmatic temperature conditions in the upper crust, salts, acids and bases will be much more associated and fluids will have lower ionic strengths (see Shmulovich *et al.*, 1995).

The solubility of quartz in H_2O has been studied intensively for over half a century (Kennedy, 1950a; Walther and Helgeson, 1977; Manning, 1994) and throughout most of the crust, solubility increases systematically with temperature and pressure (Fig. 2.7a; Rimstidt in Barnes, 1997), except at moderate temperatures (~350-550 °C) and low pressures (~< 100 MPa) (Steele-MacInnis *et al.*, 2012a; Fig. 2.7b). The solubility of quartz is modified by the presence of chloride salts, and the effect can be significant at extreme conditions of pressure and/or salinity, with both salting-in and salting-out possible (Fournier, 1985; Fournier *et al.*, 1982; Shmulovich *et al.*, 2006). Steele-MacInnis *et al.* (2012b) have shown that phase separation at upper crustal PT conditions, and the concomitant production of a high salinity brine, has an enormous effect on silica (quartz) transport and solubility, and the region of retrograde solubility in H_2O moves to higher temperatures and slightly higher pressures as the salinity of the fluid increases (Fig. 2.7b). Dissolved gases also decrease quartz solubility significantly (Walther and Orville, 1983; Newton and Manning, 2000).

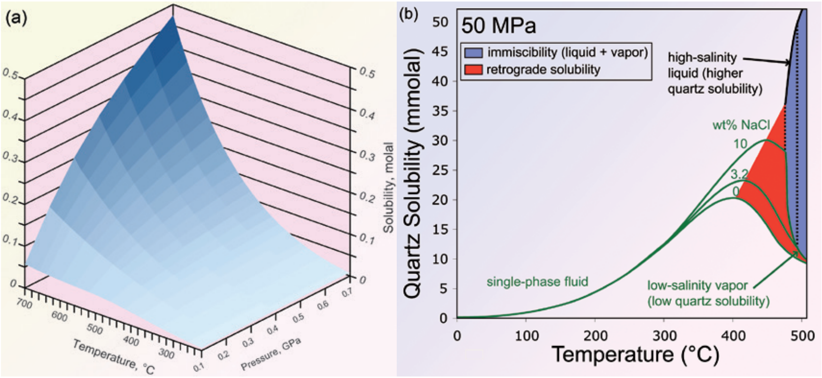


Figure 2.7 Solubility of quartz in water as a function of pressure and temperature. **(a)** Variation over crustal P-T conditions (modified from Rimstidt, 1997). **(b)** Quartz solubility at 50 MPa showing the region of retrograde solubility in low salinity fluids (modified from Steele-MacInnis *et al.*, 2012a).

Finally, it is important to remember that, however exciting the study of fluids may prove to be (and it is VERY exciting!), much of the Earth's crust at any particular time is probably dry, *i.e.* lacking a free fluid phase. All too often we assume that because deep crustal rocks formed through metamorphic dehydration reactions, they will always contain fluid, but this is not the case. Fluids are physically and chemically unstable in the deep crust; if they are unable to migrate upwards despite buoyancy, they will be consumed by hydration or carbonation reactions as the host rocks cool. This is why old rocks from the deep crust, now exposed at the surface, still preserve the story of their original formation rather than being completely recrystallised. Where fluid is present, it is not just the composition of the fluid that is important, but also the quantity of fluid that dictates what effects it will have on its host rocks. The Law of Mass Balance must be obeyed even more rigorously than the Law of Mass Action!

2.1 What Controls Crustal Fluid Compositions?

In this section, we concentrate on what is known about the dissolved load of aqueous fluids, as opposed to the proportions of fluid species themselves. Except for very shallow and active flow systems in the shallow crust, and fluids evolving from magmas, fluids react with the rocks that host them, and so their compositions reflect those interactions. If the fluid interacts sufficiently with the rocks they become a saturated solution of the host. This has been recognised for many decades, and gave rise to the thermodynamic approach to describe fluid compositions developed by *Korzhinskii* in Russia and by *Garrels* and his students in the USA. With more experimental data and the increasing computational power that became available in the 1970s, *Hal Helgeson* set about developing a consistent thermodynamic approach to minerals and aqueous crustal fluids which would allow fluid compositions to be estimated over a wide range of crustal P-T conditions. The remarkable success of the efforts of the group at “Prediction Central” – *Helgeson’s* laboratory at Berkeley – can be judged by the fact that today much of the data that underpins the various computer codes used for modelling fluid-rock interactions is still derived from *Helgeson’s* work. The details of his treatment of mineral and fluid thermodynamics were published in a series of landmark papers in *American Journal of Science*. This pioneering work (Helgeson *et al.*, 1978) has been largely superseded for minerals by new internally consistent databases, such as THERMOCALC (Powell and Holland, 1988; Holland and Powell, 1998; for the latest developments see: http://www.metamorph.geo.uni-mainz.de/thermocalc/), but the treatment of aqueous electrolytes enshrined in the SUPCRT code (Johnson *et al.*, 1992) has not yet been systematically revised. Only recently have alternative approaches been developed (Dolejs and Manning, 2010). One of the most elegant aspects of *Helgeson’s* work is that it combines a rigorous thermodynamic rationale with an empiricism that ensures that useful results are obtained even for systems that are not very well investigated. His approach to activity coefficients in aqueous electrolytes (known as the b-dot method from the symbol used) is an extended version of the Debye-Huckel theory, based on the assumption that the dominant solute in geological fluids is NaCl. It was designed to give reliable results for fluids of up to about 3M NaCl over a wide range of compositions and crustal P-T conditions. It fails to predict the behaviour of salt-saturated solutions, but the advantage over the alternative “Pitzer approach” (Pabalan and Pitzer, 1987), which does work for concentrated brines, is the much wider range of compositions and conditions for which it will give results that are often reasonable and consistent with observations.

2.1.1 Temperature and pressure

Temperature and pressure directly dictate the concentrations of fluid components when the fluid is saturated in the minerals contained in the host rock, but temperature in particular is also important in determining cation concentrations influenced by exchange reactions. Some simple and contrasting examples of P-T dependent saturation are provided by concentrations of NaCl (halite), $CaSO_4$ (anhydrite) and SiO_2 (quartz) (Fig. 2.7). Sulphate minerals such as anhydrite, and also carbonates, become less soluble with increasing temperature, *i.e.* they exhibit retrograde solubility, whereas quartz only exhibits retrograde solubility over limited regions of crustal PT space (Rimstidt, 1997).

As noted earlier, a *"second critical end point"* occurs at extreme temperature and pressure in silicate – water systems, although this is only achieved at mantle pressures. Much as the critical point in a simple one-component system (Figs. 2.1 and 2.2) marks the end of the liquid + vapour curve, beyond which only a single, supercritical fluid is possible, so the second critical end point marks the limit to immiscibility between a wet silicate melt and aqueous solutions; above this critical point the aqueous solution and the melt will dissolve in each other to create a single phase (Mibe *et al.*, 2007; Stalder *et al.*, 2000). In the crust, there is a clear miscibility gap between granite and aqueous fluid, but at mantle pressures, it appears that melts and aqueous fluids will merge, and this is likely an important factor in generating hydrous arc magmas in deep subduction environments.

2.1.2 Chloride – the master variable

The dissolved electrolyte content of crustal fluids is only rarely controlled by saturation with chloride salts. Instead, dissolved chloride concentrations vary over a very wide range, approaching and even exceeding salt saturation under surface conditions (Fig. 2.8). High salinities can be inherited from sedimentary formation waters or generated by halite dissolution or immiscibility to produce saline brines in equilibrium with a low salinity vapour (Sourirajan and Kennedy, 1962; Bodnar *et al.,* 1985a). Evaporation leads to highly saline fluids at the Earth's surface.

The idea of representing crustal fluid compositions on plots against chloride, which acts as an independent or master variable, was first popularised by *Hans Eugster*. Conventionally, aqueous geochemists dealing with surface waters consider pH to be the master variable controlling the activities of other aqueous species (*e.g.*, White, 2013), but it was apparent to geochemists such as *Helgeson* and *Eugster* who were extending solution chemistry into the rock-saturated fluids of the crust that pH is actually fixed by mineral-fluid equilibria (strictly, it is not buffered as we shall see below) whereas chloride is seldom constrained. As a result, the chloride content of crustal fluids is highly variable and dictates the total amount of dissolved cations, so that variations in solution chemistry can be represented in plots of log Cl against the log of the activities or concentrations of a wide range of metal species (Gunter and Eugster, 1980; Eugster and Gunter, 1981).

Chloride-rich crustal fluids tend to be rich in Ca relative to evaporated seawater of similar chlorinity (McCaffrey *et al.,* 1987) (Table 2.1), unless there are no sources of Ca to be leached from the host rock (as in evolved granitic fluids). The evolution of brines in evaporite systems can lead to high Ca as a result of dolomitisation (Warren, 2006), or Ca can be leached from plagioclase in crystalline rocks (see below).

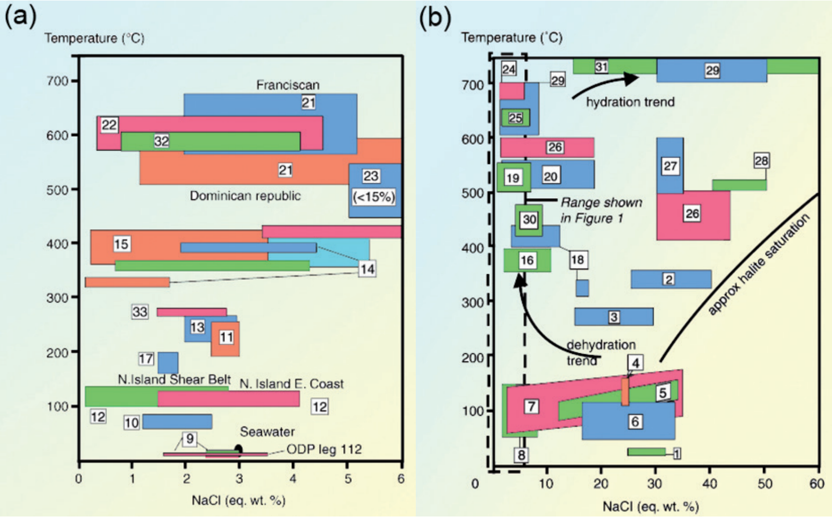


Figure 2.8 The salinity of sedimentary pore fluids and metamorphic waters for different geological settings from the compilation of Yardley and Graham (2002). Full details are in this paper. Part **(a)** is for fluids from rocks deposited in oceanic or accretionary prism settings, and is compiled from fluid inclusion measurements, with borehole data at the lowest temperatures. Part **(b)** shows data from sediments and rocks originally deposited in continental and continental margin settings. Note the much higher salinities attained by many continental margin fluids, with compositions approaching halite saturation even in some amphibolite facies rocks; the entire range of salinities recorded in part (a) lies within the dashed outline at the left of part (b). Evidence for dilution at higher temperatures due to progressive dehydration is remarkably weak, although at the very highest grades there is evidence for increased salinities ascribed to dissolution of water into melt (modified from Yardley and Graham, 2002).

There is an important consequence of the high Ca levels in saline fluids. Most other anions that are important in nature form insoluble solids with Ca; for example anhydrite ($CaSO_4$), calcite ($CaCO_3$), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) or fluorite (CaF_2). Thus, if a chloride fluid is rich in Ca, saturation with such phases will keep their associated anion concentrations low. For most crustal fluids, the cation load balances the chloride load to a reasonably good approximation.

As an aside, in igneous geochemistry it is common to think of a distribution coefficient governing the partitioning of trace elements between minerals and melt. For aqueous electrolyte solutions there is no equivalent concept and the idea of a distribution coefficient between minerals and aqueous fluids is meaningless. A saturated solution of albite in distilled water has a much lower Na concentration than a saturated solution of albite in seawater under the same conditions, simply because seawater has a much higher chloride concentration. As there is a very large range of salinities reported from crustal fluids, their metal concentrations vary accordingly (Table 2.1).

Table 2.1 Examples of crustal fluid analyses from a wide range of geological settings (after Yardley, 2013). Included are analyses of both borehole samples and fluid inclusions. See Yardley (2013) for sources.

Field/Location	Sample	Temp °C	Na	K	Li	Mg	Ca	Sr	Ba	Fe	Mn	Zn	Pb	Cu	B	F	Cl	Br	SO_4	HCO_3
Seawater		15	10670,0	399,0	0,2	1250,0	411,0	8,1							4,5	13,0	19350,0	67,3	2700,0	142,0
Black Smoker Fluids																				
13°N			10345	938	5,7	0	641	7,9		100,5	33,5						19500			
East Pacific Rise			12874	1157	4,8	0	2204	15		58,6	44						26235			
Geothermal Brines																				
Salton Sea																				
SSSDP Well 12-1985		305	53000	16700	194	33	27400	411	203	1560	1450	518	100	5,9	257		151000	99	65	
SSSDP Well 3-1986		330	54800	17700	209	49	28500	421	353	1710	1500	507	102	6,8	271		157500	111	53	
Commercial Well 10		295	41400	11800	152	33	20900	345	156	969	855	323	67	2	197		116000	78	53	
Commercial well 81		230	15000	2480	55	54	2520	112	45	86	60	11	2,6		92		31000	24	53	
Oil Field Formation Waters																				
North Sea																				
Miller		120	27650	1280		105	645	72	780	47							44260		5	2470
Ravenspurn		104	69200	1500	27	3700	25500	1100	15	160					22		142200		260	
Scott		125	40380	1840		835	5790	750	200	2,9					1		78280		46	575
Central Mississippi																				
Bay Springs Field	#3	143	63000	6150	52	2770	44600	1770	89	320	60	18	3				200400	2340	128	
Dollar Field	#19	98	47300	595	9	1150	13200	422	20	278	6	575	10				103200	950		
South Magee Field	#37	124	58200	916		2220	29900	1750	56	123	61	180	32				150300	1090	82	
Raleigh Field	#66	135	76200	979		2400	36500	2260	109	294	102	342	96				193400	1510	3	

Field/Location	Sample	Temp °C	Na	K	Li	Mg	Ca	Sr	Ba	Fe	Mn	Zn	Pb	Cu	B	F	Cl	Br	SO_4	HCO_3
Offshore Louisiana																				
	D/95	98	99600	377	6,5	963	6200	167	6	35,1	6,6	4,97			43		170000	196	116	
	F/60	68	25900	173	3,4	530	1970	70	53	7	1,2	0,06			40		44000	61	9,6	195
	G/4	132	26880	107	5,7	103	805	87	12	4,4	0,83	0,04			77		43530	38	38,7	551
Michigan Basin																				
		52,7	23000	9500		6080	60000										153000	1270		
		54,6	9820	22600	61	12800	124000	6030									263000	3020		
		29,7	39400	3320		8350	49900										168000	2230		
Alberta Basin																				
Viking 2		47	22000	102	5	416	1070	182	365	7,13	0,62	0,04			7		36100	172		
Rock Creek 1		75	8470	119	4	46	123	26	14	0,15	0,09	0,06			15		12700	28	11	
M Jurassic 2		61	23600	555	16	179	793	54	2	0,25	1,02	0,03			8		36800	113	295	
Leduc 4		42	34900	1080	23	1987	5220	198	1	0,27	0,08				48		66100	274	1240	
Leduc 5		63	50000	3640	50	5035	30000	1190	7	17,48	0,49	0,83			142		144000	1260	294	
Low Grade Metamorphic Fluids																				
Pyrenees																				
Gistain	P94-5Q	300	41871	2851	207	4086	45037	2856		3716	466	279		22	50		136284	691,7	2533	
Plan de Larri	P94-9	300	24908	2257		24043	194085	778	199	1678	182			52	190		54459	125,5		
Pic Long	55141-1	300	62213	14564	1879	1207	47637	3421	1157	2868	1773	392		348	156		187405	2793	2184	
La Glere	N90-4	300	53366	7829		155	31790	1894	384	486	656	790	187		59		155332	3063	464	
Pic de Port Vieux	54319-m	345	55187	1600	530	1065	30320	2809	1076	2539	1115	1010		171	171		131421	877	265	
Columbian Emerald deposits																				
Coscuez (in Quartz)	GG-5	320	54590	11622	2031	639	44027	1605	1064	23791	3308	573	131	115			211091	100,6	1189	
Chivor (in Emerald)	GG-11	320	116142	5888	430	1568	19151	407	198	5086	569	174	54	104			230202	27,4	352	

Field/Location	Sample	Temp °C	Na	K	Li	Mg	Ca	Sr	Ba	Fe	Mn	Zn	Pb	Cu	B	F	Cl	Br	SO_4	HCO_3
Orogenic Au-Quartz Fluids																				
Brusson, N. Italy																				
	LD659	280	17314	863	27	135	793	53	24	18	2,2	1,7	2,6	3,8	432	401	21389	104	996	
	LD671	280	17163	2526	81	85	955		68	66	4	33,5		7,5	393	208	20820	87	154	
	LD886	280	16752	985	239	129	665	54	43	120	5	34,3		25,1	560	242	19112	70	102	
Basinal Fluids from basement																				
Modum Complex, Norway																				
	DOV-1	220	17118	1032	13	27	5457	83	31	53	26	3		1	24		35661	221	86	
	IA-432	220	20516	2263	71	78	4239	107	75	164	75	18		24	71		30885	197	62	
	IA-511G	220	45707	7110	144	128	24581	1307	2163	2370	248	80		37	144		74456	297	887	
Magmatic Fluids																				
Mole Granite																				
H et al. 1992		550	78000	37000			3200	30		60000	18000	5200	3300	900			266000	420		
Leno1	1	450	130000	93000	520			46	200	170000	44000	14000	10000		650		430000			
Wolf 12	A	400	72300	45600	433			170	170	67700	19400	5200	3400	160			208500			
Cornwall																				
	54150	400	16310	4186	58	598	4411		29	9130	934	192		837	623	1540	28119	80	2051	
	2320	600	39520	13960	215	121	9619	175	137	11950	3240	1569			3974	817	106360	150	6075	
Golden Dagger	SW-89-159	500	66687	14932	266	154	29249	534	146	6809	3868	774	234	34	1194	866	171637	307	534	
East Vitifer	SW-89-156	500	68519	15910	226	137	27148	493	185	7057	3433	637	151	55	959	508	172790	308	349	
Kakkonda High-T Geothermal Brine (Japan)																				
	WD-1a	500	75000	35000			15000			32000	8000						220000			

2.1.3 Cation exchange and fluid chemistry

Probably the best known example of cation exchange between fluid and solids is the exchange of Na and K between alkali feldspars and fluid:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+ \qquad (2.16)$$

At low to moderate temperatures, there is only limited solid solution in the alkali feldspar series and coexisting albite and K-feldspar are commonly present in a wide range of hydrothermally altered rocks. Since the solid phase activities remain close to unity, the changes in the equilibrium constant for the exchange reaction track directly onto changes in the Na/K ratio of the fluid. The effect of this is that the Na/K ratio of the fluid decreases with increased temperature of equilibration with coexisting alkali feldspars, something that has been recognised for many years and applied to analysis of geothermal waters as a tool for geothermal prospecting (*e.g.,* Fournier and Truesdell, 1973; see also Fig. 2.12, below). At higher temperatures it may become necessary to make a correction for activities in the solid phase, but the K/Na ratio in the fluid continues to increase with temperature.

For plagioclase, the relationship is more complex, and Na-Ca exchange between albite and anorthite (conserving Al) gives:

$$2NaAlSi_3O_8 + Ca^{++} = CaAl_2Si_2O_8 + 2Na^+ + 4SiO_2 \qquad (2.17)$$

for which the equilibrium constant contains the term $a^2_{Na^{++}}/a_{Ca^{++}}$

For fluids of different Cl-contents equilibrated with this assemblage under the same conditions, the Na/Ca ratio must therefore vary. If chlorinity is high, so that a_{Na+} and a_{Ca++} are both relatively large numbers, Na/Ca will be relatively small and calcium chloride may even be the dominant salt in solution, as is observed in some sedimentary basins and MVT Pb-Zn deposits.

The classic experimental study by Orville (1972) demonstrated that for 1m Cl solutions at 700 °C and 200 MPa, Na is strongly partitioned into the fluid, but, as predicted by theory, this is not the case for more concentrated solutions. Shmulovich and Graham (2008) found through careful experimentation that there is a strong dependence of the fluid Na/Ca ratio on chlorinity at 500 MPa and 700 °C, with the most concentrated fluids (64 molal) showing little difference between the Na/Ca ratio of the plagioclase and the fluid. Through much of the crust albite is the only stable plagioclase and so it is exchange between albite and other Ca phases that controls Ca/Na in the fluid. In many sedimentary basins, calcite is the dominant Ca-bearing phase, and so the equilibrium constant will also include a term related to the partial pressure of CO_2.

Many minerals form solid solutions due to the presence of sites on which similarly sized cations can substitute for one another, and there is therefore potential for fractionation of these cations between fluid and mineral phases. Not surprisingly, the ratios of substituting cations in the fluid rarely match those in the solid. Fe, Mg and Mn substitute for one another in a wide range of minerals and, in principle, their relative concentrations in analysed solids should be of value for predicting cation ratios in the fluid. For example, Schulien (1980) investigated Fe-Mg cation exchange between biotite and fluid and concluded that the fluid phase is strongly depleted in Mg relative to the coexisting solids, reflecting ionic radius and the biotite structure. While it is generally true that Mg levels are almost invariably very low in natural fluids (other than seawater or evaporated seawater), the effect of redox on the solubility of Fe and Mn, discussed below, makes it difficult to directly predict metal ratios in the fluid from mineral chemistry for this group of elements. A further complication for many transition elements is the formation of insoluble sulphides. It seems reasonable to suppose that in the presence of reduced S, chalcophile elements may be strongly depleted in the fluid phase.

2.1.4 Mineral controls on pH

It is only rarely that the pH of crustal fluids is strictly buffered by the coexisting minerals. Instead, pH depends on both mineralogy and the fluid dissolved load. As an example, consider a low-Ca granite containing the minerals K-feldspar + albite + quartz, undergoing hydrothermal alteration to produce muscovite. The Na:K ratio is defined by alkali feldspar exchange, as outlined in the previous section, but the total quantity of Na + K is defined by charge balance with Cl since, to a first approximation, these 2 species dominate the cation load. Thus, for a given chloride content and P-T regime, a granite-equilibrated fluid will have specific concentrations of K and Na. The coexistence of muscovite with K-feldspar then provides a further constraint on the fluid chemistry through the equilibrium:

$$\underset{\text{K-feldspar}}{3KAlSi_3O_8} + 2H^+ = \underset{\text{Muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{Quartz}}{6SiO_2} + 2K^+ \tag{2.18}$$

which defines the K^+/H^+ ratio. Hence, more chloride-rich fluids will have higher K concentrations and thus lower pH values than more dilute fluids equilibrated with the same granitic assemblage under the same conditions. One of us calculated this for 2 limiting assemblages (Yardley, 2005) and the results are illustrated in Figure 2.9. Although this type of chloride-limited control is probably very important in many crustal settings, it is not the only possible process to affect pH. The presence of an immiscible CO_2 phase can provide a pH buffer if combined with a suitable mineral, and this is discussed further below.

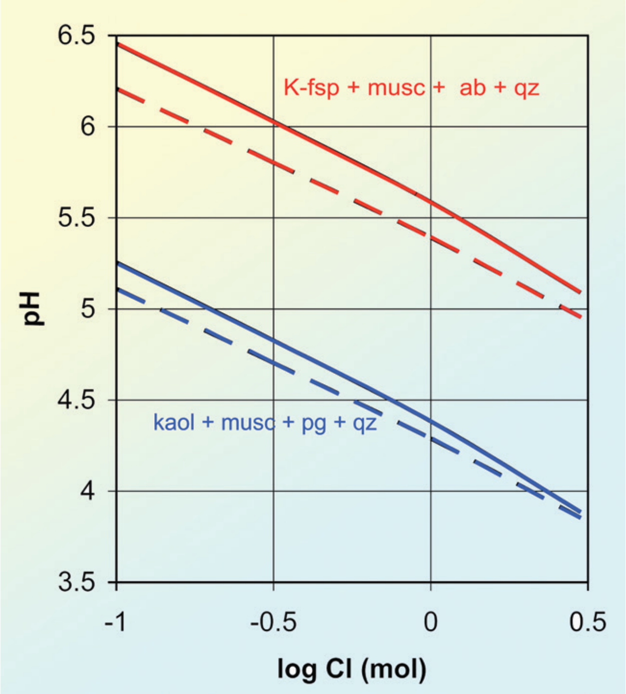


Figure 2.9 Chloride master variable diagram to show the pH of fluid in equilibrium with the buffering assemblages K-feldspar-muscovite-quartz (upper curves) and kaolinite-muscovite-quartz (lower curves) as a function of fluid chlorinity at 275 °C (solid lines) and 225 °C (broken curves) and at pressures on the boiling curve of water. At these conditions neutral pH is ca. 5.6 and pyrophyllite and kaolinite yield very similar results for the lower curves (modified from Yardley, 2005).

2.1.5 Redox controls

The redox environment has a significant influence on the solubility of metals that can exist in more than one valence state at normal crustal conditions. And, because the solubilities of different valence forms of some metals vary by one or more orders of magnitude, changing redox conditions can also be a very effective depositional mechanism for these metals. For example, Fe and Mn are more soluble under reducing conditions whereas U and Cr are more soluble under oxidising conditions; not surprisingly, the dominant depositional mechanism for most uranium ores is reduction. Crustal fluids are almost invariably strongly reduced relative to surface conditions, with hydrogen fugacities (f_{H2}) many orders of magnitude higher than oxygen fugacities (f_{O2}).

Iron is the most abundant crustal element that occurs in two different valence states, and in many rocks, coexisting Fe^{2+} and Fe^{3+} minerals buffer the oxidation state. Because of the range of environments and fluids present in the crust, redox is conventionally expressed in terms of f_{O2}, which can be defined even where water is absent. For example the hematite-magnetite (HM) oxygen buffer is:

$$\underset{\text{Magnetite}}{2Fe_3O_4} + 0.5\ O_2 = \underset{\text{Hematite}}{3Fe_2O_3} \tag{2.19}$$

This reaction defines a fugacity of oxygen that is so low under most conditions that it has no physical reality. In the presence of water, this buffer can be written to involve water as the source of oxygen:

$$\underset{\text{Magnetite}}{2Fe_3O_4} + H_2O = \underset{\text{Hematite}}{3Fe_2O_3} + H_2 \tag{2.20}$$

In this case, the reaction is written in terms of hydrogen fugacity, a parameter that is numerically much larger than the equivalent oxygen fugacity, to which it is linked by the dissociation reaction for water. And unlike oxygen fugacity, hydrogen fugacity has a meaningful physical reality and can be measured in the field. From a geothermal perspective, *Werner Giggenbach* argued that it is inappropriate to refer to oxygen fugacity because it is too small to have any physical meaning in such situations. Some have objected to this suggestion, for two reasons. The first is a practical one: if water is absent, then there is no source of hydrogen and hydrogen fugacity is undefined by the hematite-magnetite assemblage. More fundamentally however, thermodynamics does not require that a component or species actually exist, as long as its magnitude can be defined. Thermodynamics is a construct that allows us to predict what the real world would like to become, given time, but it tells us nothing about real processes. If using a parameter such as fO_2, which is physically absurd, helps remind us that thermodynamics is not about reality, then it is well worth doing.

The HM buffer defines relatively oxidising conditions by the standards of the deep crust, whereas the association of Fe^{2+} – silicates with magnetite provides a relatively reducing lower limit. In experimental studies, the best known buffer of this type is quartz-fayalite-magnetite (QFM):

$$\underset{\text{Fayalite}}{3Fe_2SiO_4} + O_2 = \underset{\text{Magnetite}}{2\ Fe_3O_4} + \underset{\text{Quartz}}{3SiO_2} \tag{2.21}$$

or:

$$\underset{\text{Fayalite}}{3Fe_2SiO_4} + 2H_2O = \underset{\text{Magnetite}}{2\ Fe_3O_4} + \underset{\text{Quartz}}{3SiO_2} + 2H_2 \tag{2.22}$$

One might guess, on the face of it, that QFM is not a particularly good approximation to common crustal mineral assemblages, as pure fayalite is extremely rare and quartz and olivine rarely coexist, but it does appear to provide a reasonable proxy for the redox controls in many natural assemblages containing Fe^{++} silicates, magnetite (or some combination of phases that can host both Fe^{2+} and

Fe^{3+}) and quartz. In ultramafic rocks (which contain predominantly forsterite olivine, of course), silica activity lies well below quartz saturation and is defined instead by enstatite – olivine coexistence. As a result of the low silica activity, f_{H2} is elevated and can be high enough to give rise to hydrogen discharges from ultramafic lithologies. With the exception of such extreme lithologies however, the fugacities of both hydrogen and oxygen in crustal fluids are sufficiently low that the buffer capacity of most crustal rocks dominates.

For a very wide range of rock types, considerable fluid fluxes are needed before one or other of the solid iron-bearing phases is likely to be consumed, so iron-bearing minerals provide an effective redox buffer from a lithocentric viewpoint. What is much harder to understand is how flowing fluids can modify the redox state of the rocks through which they pass, given the low fugacities of O_2 and H_2. Fe^{2+} is much more soluble than Fe^{3+} in chloride fluids, and so while reduced fluids can transport reduced Fe into rocks that they infiltrate, simple chloride fluids cannot effectively export an oxidised environment into a reducing one, because of the low solubility of the oxidised species. This point has been forcefully made by Frost and Ballhaus (1998), in the context of understanding why the mantle wedge and arc magmas derived from it are relatively oxidised compared to mantle elsewhere. They point out that the widely accepted explanation that water derived from the slab can act as an oxidising agent (*e.g.,* Brandon and Draper, 1996) is simply untenable. We note, however, that in some ore-forming environments, such as the roll-front uranium deposits, flowing, highly-oxidised fluids modify the redox state of the rocks to a great extent, and vice versa.

It is likely that the main fluid-mobile redox agents in the crust are S and C, since both can occur in fluids at high concentrations in more than one valence state. Additionally, at shallow levels, boiling or phase separation can lead to subsequent oxidation because boiling fractionates H_2 and O_2 into the vapour phase, and when this loss triggers further dissociation of water, the relative value of f_{O2} to f_{H2} ratio in the fluid increases significantly compared to a rock-equilibrated value, and so can trigger oxidation of wall rocks. S species are particularly potent redox agents because the valency difference between 2^- and 6^+ is so large that, for example, oxidation of 1 sulphide ion to sulphate can reduce 8 Fe^{3+} to Fe^{2+}. Coexisting iron oxides and sulphides commonly define conditions close to the sulphate – sulphide species predominance boundaries (Fig. 2.10). Unlike Fe, a range of oxidised and reduced sulphur species are soluble, and they are therefore effective at exporting redox conditions. At low temperatures, below about 100 °C, S-species react very slowly and sulphate reduction is normally biologically mediated, but thermogenic sulphate reduction becomes an important redox process at higher temperatures and has been implicated in the formation of sediment-hosted sulphide ores (*e.g.,* Thom and Anderson, 2008). Many brines in sedimentary formations contain relatively high levels of sulphate, as do some magmatic fluids, and so these fluids have considerable potential to oxidise rocks into which they infiltrate. Sulphate-rich brines may remain effectively oxidising even after deep burial if they are hosted by sediments with high porosity such that they overwhelm the reducing capacity of their immediate hosts.

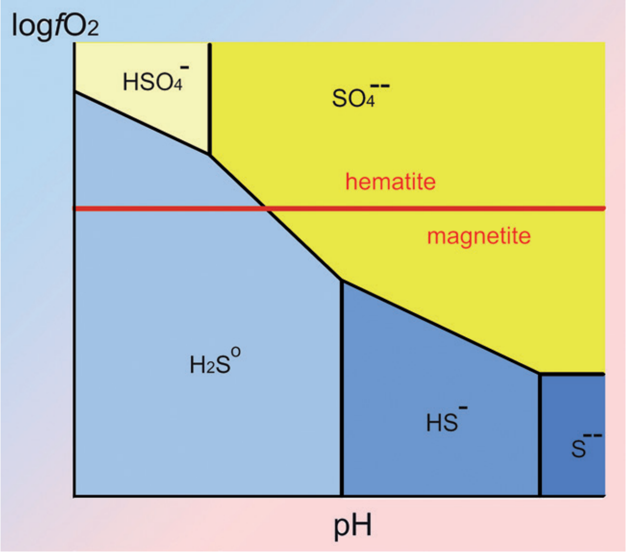


Figure 2.10 Schematic log fO_2 – pH diagram to illustrate the relative distribution of the predominance fields of the major S-species and the hematite-magnetite buffer. Under relatively acid conditions, reduced species often predominate, especially since many crustal assemblages are more reducing than hematite-magnetite, but sulphate fluids are also important in some situations.

Carbon occurs in sediments in a reduced form as organic matter, oil, gas or simply graphite, but can be oxidised to form carbonate species, CO_2 gas, and minerals. Reduced carbon is less common in medium grade metamorphic rocks than in sediments, suggesting that oxidation takes place during prograde metamorphism, possibly coupled to reduction of iron originally present as iron oxide grain coats or in other forms. Even in sediments, organic matter acts as an important reductant and it is not surprising that many sedimentary rocks provide strongly reducing environments. Veins formed by infiltration of fluid into graphitic rocks often have bleached margins as a result of oxidation of the graphite by the incoming fluid.

Manganese shows a similar reduction in solubility with oxidation to iron, but Mn remains soluble to a higher f_{O2} than Fe. *Simon Bottrell* showed that the Fe/Mn ratio of fluids from mildly oxidising rocks is commonly near or below 1, even though the rocks have much higher Fe/Mn ratios. Under more reducing conditions, Fe predominates in the fluid (Bottrell and Yardley, 1991), although fluid Mn/Fe ratios are still normally higher than those in associated rocks.

Examples of strongly oxidised environments in the deep crust are rare, but there are many examples of contrasts in redox state between different lithologies, such as those bearing hematite and others containing graphite. Examples of extensive changes of iron oxidation state are quite common in some types of ore deposits and metasomatic rocks. For example the development of epidote or hematite-rich assemblages in metabasites. As we shall see below, movement of fluids between rocks in different redox states is an important factor in the formation of a number of types of ore deposit.

2.1.6 Gas solubility in aqueous fluids

Under near-surface conditions, few gases have significant solubilities in water. Ammonia and hydrogen sulphide are the most conspicuous exceptions. Some gases, such as oxygen, hydrogen, nitrogen and the noble gases remain very insoluble in water over a wide range of crustal conditions, but others, notably carbon dioxide and, to a lesser extent, methane, become miscible with pure water under mid-to lower crustal conditions. Note, however, that if the fluids also contain significant amounts of salts, immiscibility can extend over the complete range of crustal PT conditions.

The initial dissolution of carbon dioxide in water can be written as:

$$CO_2 + H_2O = H_2CO_3 \tag{2.23}$$

and this leads to minor dissociation of carbonic acid:

$$H_2CO_3 = H^+ + HCO_3^- \tag{2.24}$$

Carbon dioxide solubility in water (and brines) is of particular interest at present, because of its applications for Geological Carbon Storage by injection of CO_2 emissions into saline aquifers. The immediate effect of the dissolution of pressurised CO_2 into pore waters is to lower pH, and in the absence of mineral interactions the resulting pH of a CO_2-saturated aqueous fluid under sedimentary basin conditions would fall below 3. However, conversion of feldspar to clays, clay leaching or carbonate dissolution all serve to raise pH (Rosenqvist *et al.*, 2012). One of us (Bodnar *et al.,* 2013b; Steele-MacInnis *et al.,* 2013) has recently examined the solubility of CO_2 in saline formations and the potential implications for implementing an effective storage protocol to accommodate the large amounts of CO_2 being generated by coal (and other fossil fuel-burning) power plants.

From an engineering perspective, relatively little attention has been given to the consequences of mineral reactions triggered by CO_2 injection, largely because there do not appear to have been major impacts on reservoir behaviour from the injections that have been carried out to date. Whether this will still be true in the longer term remains to be seen. Calcite reactivity is very fast (Pokrovsky *et al.,* 2005), and can result in increased permeability if the injected CO_2 leads to calcite dissolution. While other carbonates dissolve more slowly, they are still fast compared to most other rock-forming minerals (Pokrovsky *et al.,* 2009; Balashov *et al.*, 2013). Silicate minerals respond more slowly, and instead of dissolving they may react to produce fine-grained phyllosilicates that clog pores and inhibit fluid flow. Both types of reaction raise pH above the levels that would be expected in the absence of mineral reactions, but the faster reacting phases will inevitably dominate the initial response to injection.

2.1.7 Metal complexation

In the search for understanding the genesis of hydrothermal ore deposits, a major avenue of research has been the investigation of ways in which metal solubility might be enhanced in crustal fluids. As a result, the potential for complexing of metals in aqueous solutions has been the subject of intensive geochemical research for half a century (Barnes, 1979; Seward, 1981; Shock and Helgeson, 1988; Seward and Barnes, 1997; Sverjensky *et al.,* 1997; Oelkers *et al.,* 2009). Some work has focussed on identifying the optimum ligands to encourage mobilisation of specific metals, while other studies have concentrated on the effect of known natural ligand concentrations on metals. There are 3 major types of complexing known to be significant for crustal fluid processes, although many geochemists have good suspicions of other complexes that may prove to be important in specific circumstances as further research is carried out. These are complexing by Cl^{-}, of undoubted importance for a wide range of transition metals in particular, bisulphide complexing, predominantly of Au and to some extent Ag and Cu (Seward, 1973; Benning and Seward, 1996; Mountain and Seward, 1999; Rickard and Luther, 2006) and alkali aluminosilicate complexing (Manning, 2006) at elevated P and T.

The formation of chloride complexes has been documented experimentally for a number of important elements including Fe, Zn, Pb and Ca (Seward, 1984; Ruaya and Seward, 1986; Heinrich and Seward, 1990; Williams-Jones and Seward, 1989; Roselle and Baumgartner, 1995) and equilibrium constants are incorporated into geochemical modelling codes. Typically, progressively larger complexes are stabilised at higher Cl^{-} activities, and the concentration of a metal in solution increases with Cl concentration at a rate distinctive of the stoichiometry of the predominant complex. This provides the basis for experimental determinations of complexation but can only be applied to rocks with caution. This is because the pH of natural fluids is not buffered to a unique value by the host rock mineral assemblage but is also dependent on salinity as we described above (Fig. 2.9). One of us (Yardley, 2005) demonstrated the impact that chloride concentration can have on transition metal concentrations for rock-buffered fluids. The combined effect of the formation of additional Cl-complexes and the lowering of pH at higher chloride concentrations is a marked increase in metal concentrations in hypersaline brines, but the metal to chloride ratios are also strongly temperature dependent (Fig. 2.11).

While Cl-complexing is expected to dominate the solubility of elements such as Fe, Zn and Pb, it is also important for other elements as a result of the predominance of Cl over most other ligands in many fluids. The rare earth elements (Wood, 1990) provide an interesting example: ideally, REE are preferentially complexed by hard ligands such as carbonate, sulphate and fluoride relative to chloride. However, in many saline crustal fluids, the much greater concentrations of chloride make it likely that chloride complexing will nevertheless predominate (Haas *et al.,* 1995; Banks *et al.,* 1994).

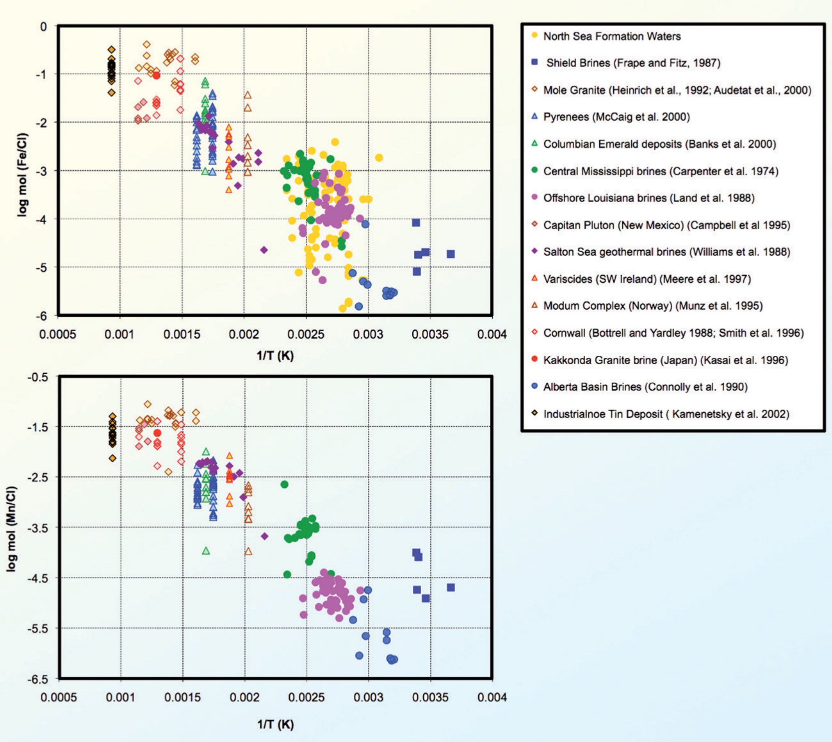


Figure 2.11 Plots of log (Fe/Cl) versus 1/T and log (Mn/Cl) versus 1/T for a wide range of crustal fluids, to demonstrate the major controls on transition metal concentrations in crustal fluids. Data include analyses of borehole-sampled waters and fluid inclusions. Fluids ranging from magmatic brines to sedimentary formation waters lie along a single trend with the metal:chloride ratio varying over nearly 6 orders of magnitude between near-surface and magmatic temperatures. Much of the scatter around the trend likely reflects variations in pH (modified from Yardley, 2005).

2.1.8 Kinetic controls on fluid compositions

Over long periods of time, it seems reasonable to suppose that fluid compositions reflect equilibrium with the adjacent host rocks for all but the most conservative components. However, at times of rapid fluid flow and most notably at lower temperature, it seems probable that the different dissolution rates of different minerals might lead to fluid compositions that reflect equilibrium with only the most reactive subset of the total host assemblage (Schott *et al.*, 2009). An excellent summary of geochemical reaction rates applied to crustal environments is provided by Rimstidt (2014). The example of CO_2 injection into formation waters has already been introduced above, and it was noted that the surface reaction rates of carbonate minerals are significantly faster than those of silicates measured under comparable conditions (Pokrovsky *et al.,* 2005, 2009; Balashov *et al.*, 2013; Kaszuba *et al.,* 2013). When injected CO_2 dissolves into formation waters, lowering the pH, the acidity is likely to be neutralised by carbonate dissolution in the first instance. This has been observed in the Frio field injection experiment (Kharaka *et al.,* 2009; Xu *et al.,* 2010), where high Ca levels were recorded at an observation well while pH did not drop to anywhere near the level predicted for CO_2 injection without wall rock reaction. Minerals often grow under far-from-equilibrium conditions and reaction products may not be the most stable phases possible, for example retrograde hydration of igneous rocks under near-surface conditions may result in partial reaction and the formation of metastable clays. In these circumstances, fluid composition probably reflects equilibrium with the actual reaction products and may differ from the composition that would result if the most stable phases were to grow.

2.1.9 Mass-limited fluids

We take it for granted that crystalline rocks have only a small amount of porosity, so that the budget of all but the most conservative elements (effectively, chloride) is controlled by solid phases (minerals) rather than by the pore fluid. In sediments however, this may not be the case. A sandstone dominantly composed of quartz may contain 20 to 30% by volume of porosity containing brine near salt saturation. These fluids are the scourge of detrital plagioclase, and are responsible for widespread albitisation of sediments, probably because they can contain so much NaCl that they convert all the original detrital plagioclase to albite without ever attaining a high enough Ca-concentration to approach equilibrium with Ca-phases. For this reason, when the fluid components are so abundant, they can swamp the contribution from minerals and are never buffered by them. *Stephanie Houston* worked with one of us (Houston *et al.,* 2011) to investigate such controls on formation waters using an industry data set in part, and coined the term *mass-limited fluids* to refer to them.

A simple example of mass-limited fluids would be those developed during diagenesis of a porous quartz reservoir sandstone containing a saline brine as pore fluid. If the sandstone is reasonably porous the rock might contain 15% brine by weight, perhaps corresponding to c. 3 wt% NaCl in the rock + pore fluid. Not only does the rock contain no significant Cl in its solid phases, it contains little Na, K or Ca. Even if it contains a few percent sodic plagioclase, this could be completely albitised by interactions with the pore fluid while leaving the pore fluid still dominated by Na.

Examples of fluids behaving in this way are not limited to NaCl-dominated brines: bittern brines may contain sufficient Mg to completely convert calcite limestones to dolomite without ever reaching calcite-dolomite equilibrium.

Figure 2.12 (modified from Yardley, 2013) shows the variation in the K/Na ratios of crustal fluids and demonstrates a particularly large range in the composition of formation waters. Brines derived by dissolution of evaporites have very low K contents and K/Na ratios, while bittern brines have exactly the opposite characteristics. Neither are close to equilibrium with coexisting alkali feldspars, not because of a failure of the mineral-fluid reaction to reach equilibrium, but because the buffering assemblage is not present; either it was not present at the outset (*e.g.*, in limestone), or one feldspar has been consumed completely by metasomatism.

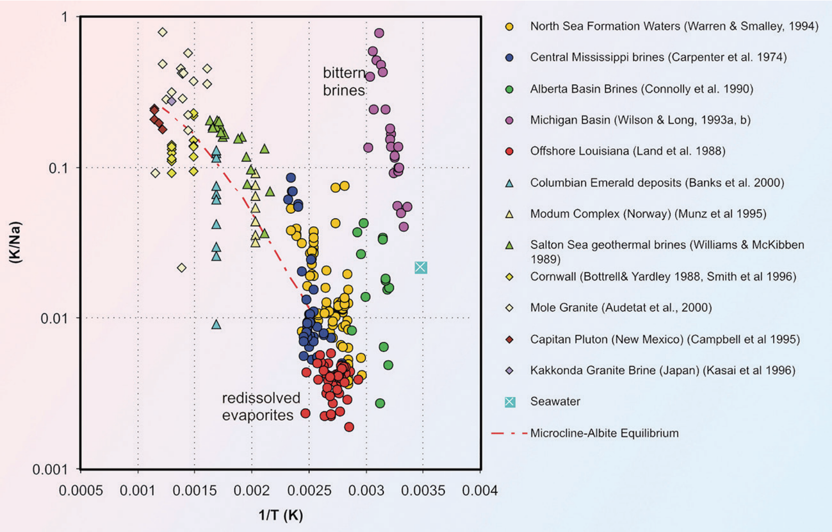


Figure 2.12 Plot of log (K/Na) versus 1/T for a range of natural crustal fluids from the data set used to compile Figure 2.11, with the microcline – albite equilibrium curve (dashed line) for comparison. Not all the fluids are from host rocks that contained coexisting plagioclase and K-feldspar, but while the high temperature data generally follow the equilibrium trend, sedimentary formation brines can deviate from it very significantly according to their origin and whether they have been able to interact with sufficient feldspar in the subsurface. As a result, different basinal brines could cause either albitisation or K-feldspathisation in the sub-surface (modified from Yardley, 2013).

From the point of view of deeper crustal processes, mass-limited brines derived from sedimentary basins are potential agents for metasomatism of underlying basement rocks. There are large terrains such as parts of the Scandinavian Shield or the Mary Kathleen district in Queensland (Oliver, 1995; Putnis and Austrheim, 2010; Rubenach, 2013) in which there has been widespread late-stage albitisation of a range of crystalline rocks. This is quite difficult to account for in terms of feldspar-buffered fluids moving from low to high temperature environments, as very large fluxes would be required to produce the requisite effects. Furthermore, there are comparable examples of metasomatic alteration in which K-feldspar dominates. Infiltration of dense, highly saline, mass-buffered brines from an overlying basin provides a simple alternative explanation for such phenomena.

2.2 Fluid Tracers: Conservative and Non-Conservative Components

Identifying the sources of the fluids is an integral part of any study of fluid processes. In studies of shallow fluid processes, it is usually possible to identify the source of fluids infiltrating the system through some distinctive isotopic or chemical characteristic. *Don White* of the USGS was an early pioneer in this area, and his classic diagram which led to the more extensive synthesis by Sheppard (1986), shown as Figure 2.13 is still used today when discussing possible fluid (water) sources in crustal environments (White, 1957). The initial recognition by Craig *et al.* (1955) that geothermal spring waters are derived from local precipitation, rather than being of magmatic origin, was revolutionary. More extensive work summarised by Sheppard (1986) has now shown that continental geothermal waters have the δD values of local precipitation, but $\delta^{18}O$ values that are distinctly heavier; the water isotopic compositions lie to the right of the meteoric water line on Figure 2.13. This pattern reflects the relative proportions of the components in water and host rock. In the water-rock system, the largest proportion of the oxygen is contained in the rock, whereas the largest proportion of the hydrogen is contained in the fluid. When reactions take place between water and host rocks, breaking down high-T minerals and forming new ones, oxygen and hydrogen atoms are exchanged between the water and the rocks. Because most of the oxygen in the system is in the rocks, the oxygen isotopic composition of the water begins to change with small amounts of water-rock interaction. However, even after quite extensive fluid-rock reaction, the δD value of the fluid is unchanged because the rock contains too little H to significantly modify the δD of the water. Taylor (1978) used these isotopic shifts to infer the water/rock ratio in hydrothermal systems.

Oxygen (and hydrogen) isotopes are one of the most widely used techniques for identifying fluid sources, but as the data from geothermal fluids show, fluids change their isotopic composition readily by interaction with minerals. Sheppard (1986) identified a distinctive stable isotope range defining metamorphic waters, but many authors fail to appreciate that this means waters that have equilibrated with silicate rocks under crustal conditions, as well as waters derived by metamorphic dehydration. In this *Perspectives*, we use the term metamorphic fluid to denote fluids that are present in rocks undergoing progressive prograde metamorphism, and therefore are derived in large part from mineral reactions.

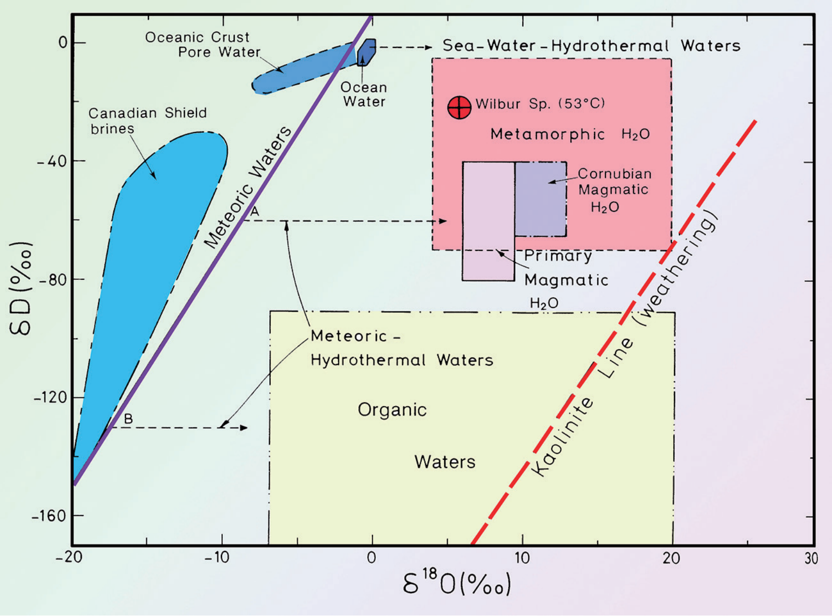


Figure 2.13 Stable isotope compositions of natural waters of different origins. The hydrogen and oxygen isotopic compositions of meteoric waters and ice are closely correlated and lie along the Meteoric Water Line. Magmatic fluids are notably enriched in ^{18}O and occupy a field to the right. Under most conditions, fluid-rock interactions in diagenesis, hydrothermal alteration and metamorphism result in waters that are similarly to the right of the meteoric water line, but Canadian Shield Brines have a distinctive composition enriched in ^{2}H that may reflect extensive closed-system mineral reactions at low temperature. Waters that have interacted with organic matter or hydrocarbons can acquire a distinctive light H signature (modified from Sheppard, 1986).

Components that are concentrated in the fluid rather than in the rock, and are therefore not greatly modified by fluid-rock interactions, are termed conservative components, and these make the best tracers of fluid origins. Apart from H, two of the more important examples of conservative components are Cl and Br (Bohlke and Irwin, 1992), but other components can behave in a conservative manner depending on fluid chemistry. For example, in brine systems, isotopes of both Pb (Doe and Stacey, 1974) and Sr (Banks *et al.,* 1991) have been used as tracers in focussed flow systems where these metals are being introduced. Where sampling is possible, the noble gases also provide very effective conservative tracers, distinguishing between surface, crustal and mantle fluid contributions (Ballentine *et al.,* 2002).

3. THE SOLVENT PERSPECTIVE: WHERE DO FLUIDS OCCUR IN THE CONTINENTAL CRUST?

3.1 Sources and Sinks of Fluids

Fluids in the crust may be locally-sourced and/or indigenous to the enclosing rocks. Examples include pore waters in sedimentary rocks or fluids released by dehydration reactions or exsolved from melts. In addition to the fluids that are buried with their host sediments or released from nearby minerals or melts, fluids can also be externally sourced, for example by deep-penetration of surface waters or by migration from relatively highly-pressured reservoirs, such as deep basins, into underlying or adjacent rocks with lower hydraulic heads. Magmas derived from the lower crust or mantle, especially those generated above the subducting oceanic lithosphere, provide a major pathway for the transport of deep fluids into the upper crust, and in some circumstances, mantle fluids may even penetrate the crust directly (*e.g.,* Pili *et al.,* 1997).

We understand the properties of fluids in sedimentary basins reasonably well. Sediments near the surface have porosities that may exceed 50%, and fluid pressure can correspond to the hydrostatic pressure. Porosity decreases with depth, although in a way that varies considerably between basins, and for a variety of reasons, overpressures develop with increasing depth (Bredehoeft and Hanshaw, 1968; Osborne and Swarbrick, 1997). Overpressured sediments often retain higher porosities than normally-pressured sediments at similar depths because the lower effective stress (the difference between confining pressure, which is a function of depth, and fluid pressure) inhibits compaction. During burial, diagenesis becomes increasingly important for reducing porosity and permeability through new mineral growth (Worden and Morad, 2000; Oelkers *et al.,* 2000).

Figure 3.1 is a schematic representation of the way in which the water content of some typical lithologies found in a sedimentary basin fill might be expected to change with burial, compaction and heating. During early stages of diagenesis, while many sediments retain a significant permeability, fluids may be replaced rather than simply expelled, and this is discussed in more detail below. Fluids may also penetrate rocks along joints and other fractures into upper crustal rocks, adding to and modifying the fluid inventory. Fluids continue to be released from mineral lattices during advanced diagenesis and metamorphism, and sedimentary formation waters become progressively less abundant and more chemically evolved as they develop continuously into what we would refer to as "metamorphic fluids".

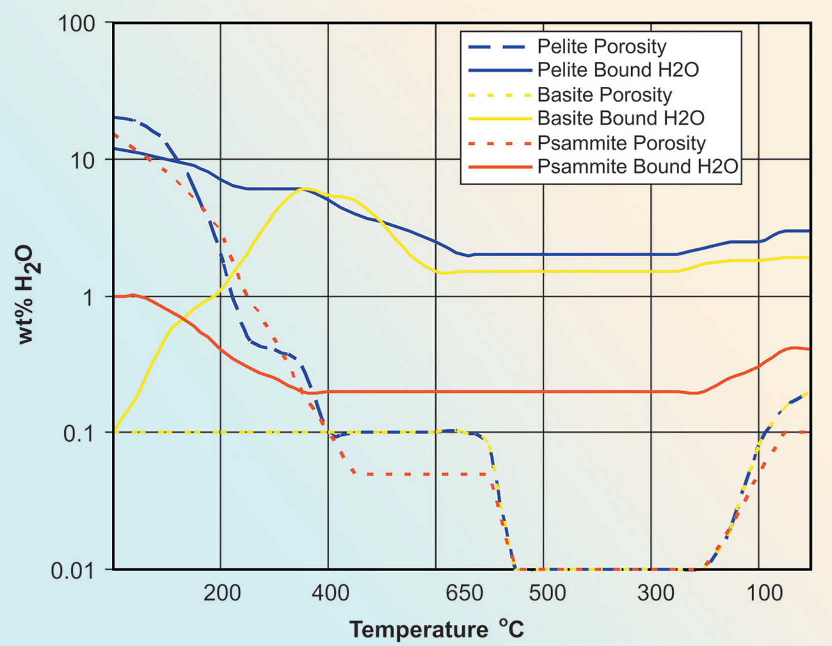


Figure 3.1 Schematic representation of the changes in water content of rocks of pelitic, psammitic and basic composition through a cycle of burial, metamorphism, uplift and retrogression. Separate curves are shown for water present in pores and in minerals for each lithology. The initial stages of burial primarily result in expulsion of pore water, and the bound water content of basic igneous rocks is actually likely to rise due to hydration. Under low grade metamorphic conditions, bound water predominates, even for psammitic rocks, and further heating results in release of water from breakdown of hydrous minerals. During uplift, the development of brittle fracture and influx of water permitting retrogression results in a small increase in water content (modified from Yardley, 2009).

One of the most puzzling aspects of the way that pore fluids evolve with the onset of metamorphism, is that fluid inclusion studies indicate that metamorphic fluids are often of comparable salinities to formation waters, whereas it might be expected that they would be diluted by release of structurally bound water from minerals (Yardley and Graham, 2002) (Fig. 2.8). This effect is much too common to be linked to the presence of evaporate beds in metamorphic sequences, although that does provide an explanation for some rare, hypersaline metamorphic fluids (Rich, 1979). At present the only explanation that I (BY) am aware of for this unexpected observation is that rocks undergoing metamorphic dehydration may develop a dual porosity, with fine cracks along some grain boundaries providing preferential flow paths. If this is the case, water released by mineral dehydration may escape rapidly along the interconnected grain boundaries without interacting with all the existing metamorphic fluid. As a result, more saline fluids may continue to reside in the less-well interconnected part of the porosity system, such as in fluid inclusions.

Magmas inevitably contain dissolved volatiles, and release of fluids from crystallising melts into their country rocks is also a locally-important source of fluids. This is especially important in shallow crustal settings, whereas in the deeper crust the magmas generally crystallise without reaching volatile saturation, and the volatile species are incorporated into minerals (hydrous phases, carbonates, sulphides/sulphides). It was noted previously that most of the water that circulates in near-surface, high-temperature geothermal fields is derived from local rainfall, but the same may not be true for all the volatile components (or the metals) of geothermal fluids. Certainly the thermal energy to drive the geothermal system is magmatically derived in most cases, and helium isotope studies of continental geothermal systems show variable deep (mantle) and crustal input into the systems (Kennedy and van Soest, 2007). Moreover, high levels of As, Sb and reduced S in geothermal waters such as the famous Champagne Pool at Ohaaki, New Zealand (Fig. 3.2) are undoubtedly of magmatic origin, even if the local precipitation has diluted the magmatic water component beyond recognition. At depths of a few kilometres, fluids released from magmas are recognised as playing a major role in the formation of porphyry-Cu, Fe-oxide – Cu – Au and some other types of ore deposit, especially acting as the source of metals (Bodnar, 1995b), even though later circulation of heated meteoric waters has also often taken place and overprinted the magmatic fluid processes. As noted by Norton (1984) and many others, over the lifetime of a magmatic-hydrothermal system associated with an epizonal pluton in the continental crust, the amount of meteoric water that circulates through the cooling pluton is on the order of 10 to 100 times the amount of magmatic water that is exsolved from the magma.

A third process that introduces fluids into the crust is when surface waters flow into crystalline rocks directly or via overlying sediments. There are many examples from within and around mountainous regions today of flow systems that involve the movement of surface water through crystalline rocks before returning, heated to the surface. The flow system in the Rhine graben, driven by the hydraulic head of the western Alps (Illies and Greiner, 1978; Person and Garven, 1989) is of this type and has been investigated at depth through geothermal drilling at Soultz-sous-Forets, north of Strasbourg (Smith *et al.,* 1998). Hot springs in high mountain valleys are similarly the result of deep-penetration of meteoric waters circulating under the influence of large topographic variations. The site of Goldschmidt 2001, at Hot Springs, Virginia in the Appalachian Mountains, gained its fame from the hot springs that result from the circulation of surface waters to great depths along deeply penetrating faults, later to be returned by rapid flow to the surface before cooling. The penetration of fluids from overpressured sedimentary basins into underlying crystalline rocks is most clearly recognised where hydrocarbons are introduced. Examples exist of hydrocarbons or their derivatives (bitumen, methane) occupying late fractures or fluid inclusions in basement rocks close to major unconformities (Munz *et al.*, 1995, 2002; Gutmanis, 2009).

Figure 3.2 Champagne Pool, New Zealand. The colourful colloids of S, As and Sb serve to demonstrate that, although much of the geothermal water originated as local rainfall, the high concentrations of many other elements require a magmatic origin.

Because of their low densities compared to the surrounding rocks, fluids are buoyant relative to their surroundings and tend to migrate upwards through rocks, unless prevented by impermeable barriers. Where flow has been focussed through specific layers, there is a chance that it will leave a trace that can be read today, but background deep flow rates of metamorphic fluids are inevitably very slow, because, as we shall see below, dehydration rates are slow. In the upper crust, fluid pressures are close to hydrostatic and fluid may convect in response to density differences due to heating or dissolution of solutes (Baker, 2007; Dreisner, 2010; Nordbotten *et al.*, 2005; Golding *et al.*, 2011), or move in response to topographic heads (Ingebritsen *et al.*, 2006). However, even within sedimentary basins, significant fluid overpressures often develop beneath cap rocks and in prograde metamorphism it is likely that fluid pressure approaches lithostatic pressure. In an overpressured system fluid can flow downwards as well as upwards as it follows more permeable layers towards points of lower hydraulic head. Figure 3.3 is a schematic to illustrate the range of hydraulic heads that might be expected in a deep basin and its basement. The rapid increase in hydraulic head with depth in an overpressured system makes it clear that deep rocks undergoing metamorphism cannot in general be infiltrated by fluids derived from shallower levels, except in special circumstances where fluid pressure has dropped well below lithostatic pressure. This provides an important constraint on the extent to which deep rocks can experience infiltration and metasomatism during metamorphism: essentially fluid release is irreversible and rocks deep in a succession undergoing metamorphism are unlikely to experience fluid infiltration during metamorphism because possible sources of fluid are limited in volume and mainly lie at (shallower) sites of lower hydraulic head. As we shall see later, this physical constraint is apparently in direct contradiction to some results from petrological calculations, a source of continuing controversy within the metamorphic petrology community.

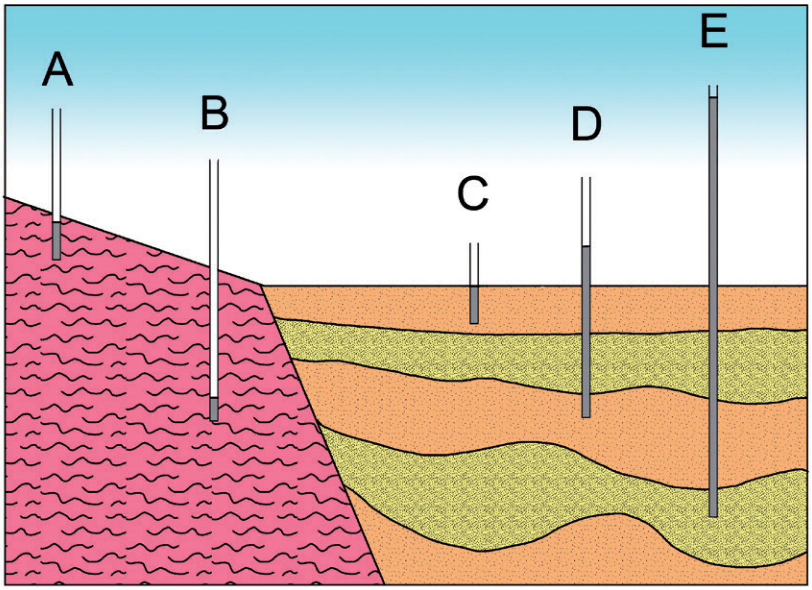


Figure 3.3 Schematic representation of the concept of hydraulic head applied to overpressured basins and underpressured crystalline basement rocks. Wells A and B are situated in crystalline rocks, and while the water level in A reflects groundwater in open fractures and corresponds to the shallow water table, the level in B is suppressed. This is a result of water being consumed by retrograde hydration reactions at a significant rate (*e.g.,* Stober and Bucher, 2004). Wells C, D and E are into progressively deeper parts of a subsiding sedimentary basin. While the shallow well again has a water level corresponding to the water table, the deeper wells have elevated water levels due to the development of overpressures beneath impermeable layers at depth. Comparison of the different wells demonstrates that water deep in an overpressured basin may rise to the surface or be driven into adjacent crystalline basement rocks (modified from Yardley, 2009).

If deep metamorphic fluids are able to migrate into the upper crust they are likely to be overwhelmed by the much larger fluid fluxes in the shallow, hydrostatically-pressured parts of the crust (Bodnar *et al.,* 2013a) and as a result there are few settings in which metamorphic fluid contributions can be recognised in surface waters today. Perhaps active geothermal fields such as Larderello in Italy, where deep contact metamorphic fluids may be entrained in the shallow convective system are the best candidates (Boiron *et al*., 2007). This makes crustal-scale metamorphic fluid processes challenging to study: it is clear that overall the metamorphic cycle drives progressive and extensive fluid loss from sediments, but it has proved very difficult to track.

3.2 What Controls the Chemical Potential of Fluid (solvent) Species in the Crust?

There are few more fundamental issues for fluid studies than determining the chemical potentials of the major fluid (solvent) species, or their activities relative to some ideal reference state. Indeed, it is the activity of solvent species that allows us to predict how a given fluid will interact with the rock, and the mineral phases that will result from this interaction. The chemical potentials of water and carbon dioxide in a rock are linked, of course, to pressure, temperature and, if a free fluid phase is present, to fluid composition. In a fluid-absent rock containing a mix of hydrous (or carbonate) minerals and their anhydrous (or uncarbonated) equivalents, the water and carbon dioxide activities are buffered by the mineral assemblage (Yardley and Valley, 1997) as explained below. Once again, it is helpful to remember that we are dealing with thermodynamics rather than reality.

Except during rapid flow events, it is reasonable to assume that fluid temperature is the same as the host rock temperature. Fluid pressure is more complex and Earth Scientists conventionally use one of two possible end members. For rocks that have reasonably interconnected permeability extending to the surface, then fluid pressure is assumed to be hydrostatic, that is, it is defined by the weight of the overlying column of water. Of course, rock is much denser than fluid, which means that the lithostatic pressure acting on the rock is greater than the fluid pressure by an amount given by the density ratio and depth. This pressure difference acts to shut down the pores and fractures that contain fluids, but whether or not it is successful depends on rock strength. For a rock that retains open pathways so that the fluid pressure is hydrostatic, the chemical potentials of fluid species depend on hydrostatic pressure, temperature and fluid composition.

Hydrostatically-pressured fluids are routinely encountered by drilling, but at high temperatures or in weak rocks such as sediments the pressure differential cannot be maintained and as pores and fractures collapse, fluid pressure increases to approach lithostatic values (Osbourne and Swarbrick, 1997). Any system in which fluid pressure exceeds hydrostatic pressure is said to be overpressured, and because the overpressure provides a hydraulic head pushing fluid out, it is generally seen as a dynamic phenomenon with ongoing pore collapse and fluid generation balancing the loss of fluid (Neuzil, 1995). Where a free fluid phase is present, chemical potentials of fluid (*i.e.* solvent) species depend on P_{fluid}, T and fluid composition, and so vary significantly between hydrostatically-pressured and lithostatically-pressured regimes.

In the absence of a free fluid, the chemical potentials of the solvent species are likely to be fixed (*i.e.* buffered) by mineral equilibria. Since they are thermodynamic values, they carry no physical implications as to how the fluid occurs. A simple example of a reaction that buffers the chemical potential of water is the dehydration reaction of muscovite:

$$\begin{gathered} KAl_3Si_3O_{10}(OH)_2 + SiO_2 = Al_2SiO_5 + KAlSi_3O_8 + H_2O \\ \text{muscovite + quartz = kyanite + K-feldspar + water} \end{gathered} \tag{3.1}$$

Provided all the minerals in a partially retrogressed kyanite-K-feldspar rock are in equilibrium, there is a simple energy balance between the Gibbs free energies of the solid phases that serves to define the chemical potential of water (G_{H_2O}):

$$G_{H_2O} = -\Delta G_s = (G_{K\text{-}fsp} + G_{ky}) - (G_{musc} - G_{qz}) \tag{3.2}$$

In this equation, ΔG_s is the difference between the Gibbs Free Energies of the solid phases at the PT conditions of interest, as defined in the final part of the equation using the common mineral abbreviations for the phases listed. It is reasonable to suppose that equilibrium will indeed be approached over the long time scales in which crystalline rocks can reside in the crust, at least at temperatures exceeding a few hundred degrees, and so at depths of more than around 10 km, equilibria like this will define the chemical potential of water within the rock, even in apparently unreactive crystalline rocks.

In summary, there are three endmember conditions that can define the chemical potential of fluids in crustal rocks, each representing a possible equilibrium condition. Hydrostatic fluid pressure is an effective definition at shallow crustal levels, including shallow sedimentary basins and active geothermal fields. In fractured basement rocks it may serve to define the chemical potential in interconnected fractures, but is not relevant to the state of the blocks of solid, more or less impermeable rocks that lie between them. Lithostatic fluid pressure is the other endmember for fluid-saturated systems and is the dominant constraint where rocks can compact, minimising porosity, are heated so that fluid expands, or are undergoing devolatilisation reactions. Here, the rate of fluid escape is balanced by the rate of fluid generation and expansion, and porosity collapse. Thermodynamically buffered chemical potentials prevail in crystalline rocks cooled below their peak temperature, where the products of partial retrogression coexist with their higher grade parents and a free fluid is no longer present. Figure 3.4 illustrates the very different values for the fugacity of water that might obtain at a similar depth in the crust according to which of these mechanisms is operative.

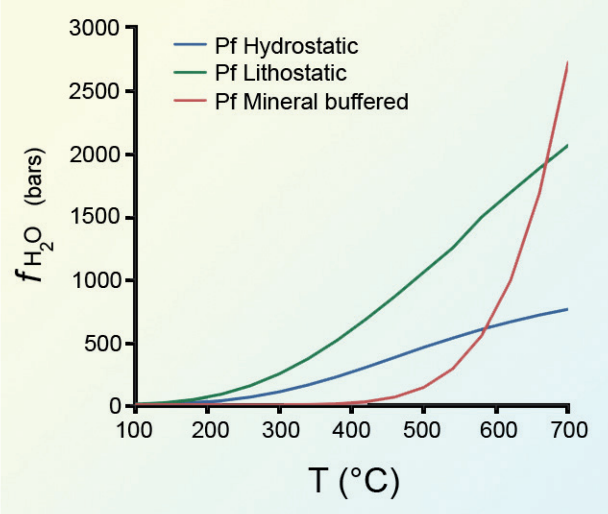


Figure 3.4 Fugacity of water as a function of temperature along a geothermal gradient of 30 °C/km, calculated for each of the possible fluid equilibrium states discussed in the text. In the case of water at hydrostatic or at lithostatic pressure, the fugacity (from Burnham *et al.*, 1969) increases progressively with depth of burial. In a basin such as that shown in Figure 3.3 it will shift up from the hydrostatic curve to the lithostatic curve at relatively low temperatures, with the development of overpressure. The mineral-buffered case has been calculated for the case of coexisting muscovite + quartz + K-feldspar + sillimanite along the geotherm with data from Helgeson *et al.* (1978). The point where the mineral-buffered and lithostatic-pressure curves cross corresponds to the effective upper T limit of muscovite + quartz along this geotherm, as at higher temperatures hydrofracturing would take place.

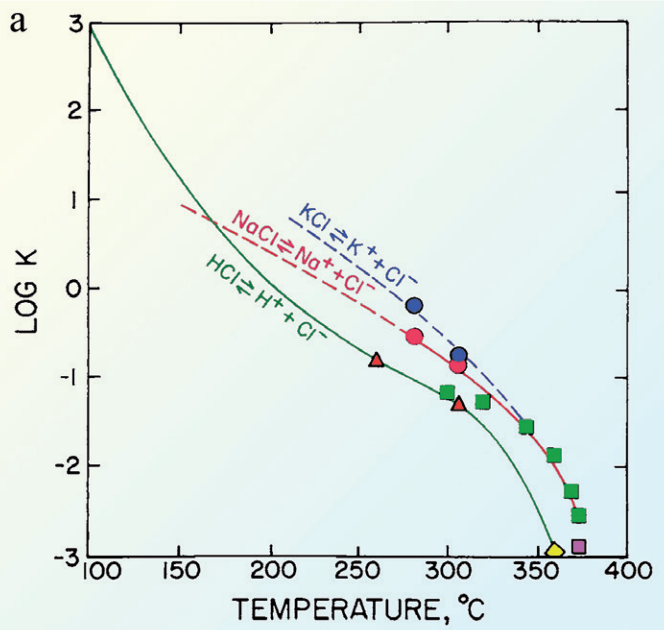
3.2.1 The influence of dissolved load on the chemical potentials of fluid species

High solute concentrations reduce the mole fraction of water in an aqueous fluid, and so lead to a reduction in water activity. Most commonly, this effect is neglected, and indeed it is quite small, for most saline formation waters in the upper crust. However, there are circumstances where the impact of the dissolved load on water activity is significant, because the mole fraction of water in the fluid is significantly reduced. Under hot, shallow conditions, water has a relatively low density and low electrical conductivity (Quist and Marshall, 1968) because dissolved salts tend to form ion pairs, but where hot water is denser, at higher pressures, conductivity is higher and dissociation can be more or less complete even at high temperatures. The mole fraction of water (X_{H2O}) is given by the relationship:

$$X_{H2O} = n_{H2O}/(n_{H2O} + \Sigma ni) \tag{3.3}$$

where n_{H2O} refers to the number of moles of water in the solution, and Σn_i is the sum of the number of moles of all the i species in solution. For a given solution, if the solute is in the form of ion pairs, this value will be larger than if the ion pairs have dissociated. For example, for conditions under which NaCl is fully associated, a fluid with an equal number of moles of water and NaCl (≈74 wt.% NaCl) will have $X_{H2O} = 0.5$. If, however, the temperature conditions change so that the fluid dissociates, $X_{H2O} = n_{H2O} / (n_{H2O} + n_{Cl-} + n_{Na+}) = 0.33$. In the case of divalent chloride salts, the effect can be even more extreme. Data for dissociation of salts at low pressures, compiled by Helgeson (1969), are shown in Figure 3.5a and indicate strong association at high temperatures, but it is now clear that salts do dissociate at high pressures, even at high temperatures, and this reduces the activity of water in saline fluids to a significant extent. This was demonstrated experimentally by Shmulovich and Graham (1996) based on the effect of salt on the dehydration of brucite. Similarly, Aranovich and Newton (1996) demonstrated the effect of salt and the concomitant lowering of water activity on the melting of albite, relative to the effect of added CO_2 on water activity (Fig. 3.5b,c).

Highly saline brines are quite widespread in nature. They can arise by salt dissolution or by removal of water from brines through hydration reactions. They can also be produced via fluid immiscibility over a wide range of PT conditions, and they can reach extreme enrichment in a range of metals (Svensen *et al.*,



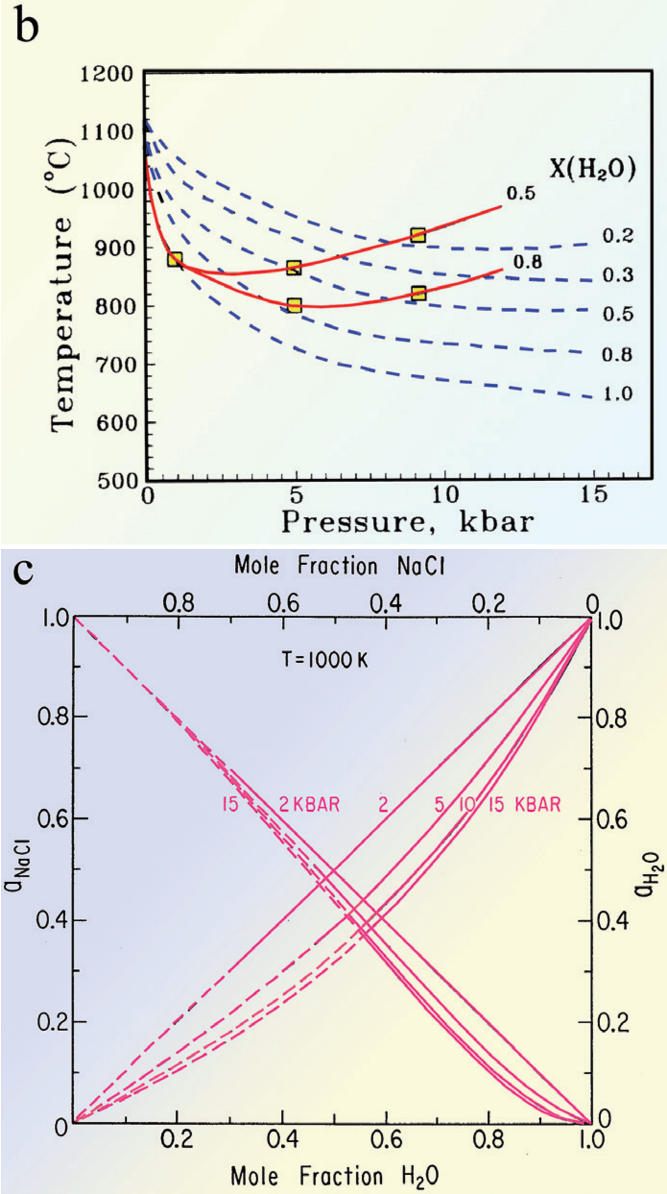


Figure 3.5 Dissociation of salts as a function of P and T and their effect on melting and dehydration at elevated pressures. **(a)** Shows dissociation constants at temperatures along the boiling curve (modified from Helgeson,1969) and shows a strong increase in the degree of association of chloride salts with increasing

temperature and decreasing fluid density. **(b)** Contrasts the melting temperature of albite in the presence of H_2O-CO_2 fluids (dashed lines) with melting temperatures in H_2O-NaCl fluids (solid lines) (modified from Shmulovich and Graham, 1996). Numbers denote notional XH_2O. For H_2O-CO_2 fluids there is no major change in speciation with pressure and increased pressure invariably results in a decrease in melting temperature. H_2O-NaCl fluids show a similar trend at low pressures but with at higher pressure the melting temperature rises with increased pressure, as discussed in the text. **(c)** Shows an analogous effect deduced from the effect of salt on the dehydration of brucite at 1,000 K (modified from Aranovich and Newton, 1996). At low pressures, H_2O and NaCl behave almost ideally, but at elevated pressures the activity of water is significantly lowered relative to the mole fraction, and this can likewise be attributed to the effects of increasing dissociation of NaCl to higher pressures.

1999; Campbell *et al.,* 1995). The examples studied experimentally by Aranovich and Newton (1996) and Shmulovich and Graham (1996) were at relatively high temperatures (>600 °C) and lower crustal pressures to produce lowered water activities. The verification of this process identified for the first time a mechanism to generate aqueous solutions capable of producing metasomatic effects operating in the granulite facies (T > 750 °C) where most rocks begin to melt in the presence of water-rich fluids (Fig. 3.6). Earlier work had invoked CO_2 as the component that allowed the persistence of fluids in granulites (Touret,1981), but while H_2O-CO_2 fluids have low water activity, they also have very low metal carrying capacity. The low solubility of most ionic species in CO_2 has been cited as evidence that CO_2 alone cannot be responsible for some features observed in granulite facies metamorphism, including alkali-exchanged feldspars (Na^+ with K^+) in charnockites, garnet corrosion textures, synmetamorphic quartz veins, the apparent mobility of Ca, Fe, Mg, and REE, and depletion of Rb and Th (Newton *et al.*, 1998). The discovery that, at granulite facies conditions, brines combine very low water activities with large dissolved loads has provided a reconciliation of apparently contradictory evidence for metasomatism by fluids under conditions where rocks undergo partial melting at moderate to high water activities.

While thermodynamic models for predicting activities of various fluid components have evolved and improved significantly in recent decades, we are still far away from having valid models for all fluid components over the complete range of crustal PTX conditions. Laboratory experimental studies provide the fundamental information needed to build and test thermodynamic models. During the time when we were students and young professors (and for several years before), there were many world-class facilities generating basic experimental data under carefully controlled PTX conditions. Today, the researchers who led these efforts are mostly retired or (unfortunately) deceased and their world-class laboratory facilities have been shuttered. But, all is not lost, as a new generation of young active researchers has taken up the gauntlet, using modern state of the art techniques such as various synchrotron-based spectroscopies (XRF, XANES, XAFS, FTIR, Raman), often combining the hydrothermal diamond anvil cell with these instruments to study fluids *in situ* at high temperatures and pressures.

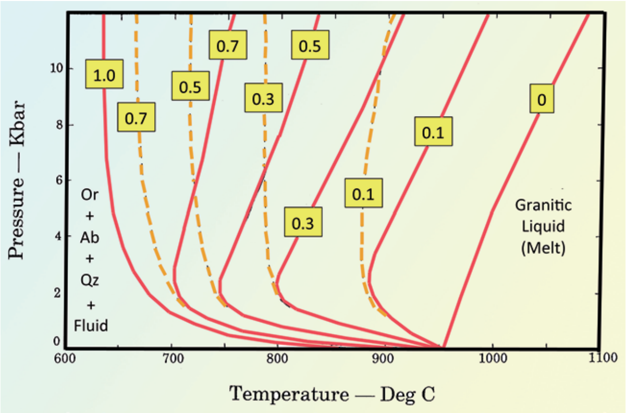


Figure 3.6 Solidus curves in the simple granite system $KAlSi_3O_8$ (Or) – $NaAlSi_3O_8$ (Ab) – SiO_2 (Qz) – H_2O for NaCl solutions of fixed X_{H2O} (solid lines), calculated from activity-concentration relations in the NaCl – H_2O system, and corresponding X_{H2O} curves (dashed lines) in the system CO_2 – H_2O (dashed) from Ebadi and Johannes (1991) (modified from Aranovich and Newton, 1996).

3.3 Fluid Flow Paths through Rocks

From a petrological viewpoint, we generally think of chemical potential varying with fugacity and hence fluid pressure, but it also follows hydraulic head – the parameter that rigorously defines where fluids will flow. Seen in terms of hydraulic head, there are some immediate and general points that come out of the 3 end-member analysis of fluid systems described in the previous section. Hydrostatically-pressured systems do not impose limits on the amount of fluid that can move through them unless the head is drawn down in response to flow. Temperature variations or topographic head gradients can drive very large fluid fluxes over long periods of time, until the driving force is dissipated or the flow paths are obstructed by mineral precipitates. In contrast, overpressured reservoirs can only leak fluid, they cannot be recharged except from more highly overpressured reservoirs. While the existence of overpressure makes it possible to have catastrophic and explosive fluid release when the system is breached, the loss of overpressure shuts down porosity and closes fractures making it hard to replace the fluid by infiltration. Fluid loss can be very rapid but recharge is likely to be slow.

An additional complication is that fluid pressure regimes vary through geological time. Extensional faulting creates new space with a very low initial hydraulic head into which fluids will be sucked from surrounding rocks, but faulting can also lead to the local expulsion of fluid from fractures, which then become closed. This process has been documented for crystalline rocks near the surface by Muir-Wood and King (1993).

It is a common sense observation that in the shallow rocks and sediments from which we extract water and on which we build our houses, water moves in very different ways depending on the rock types present. In many sedimentary rocks, fluid moves through the interconnected pore spaces that occur throughout the rock, while in shallow crystalline rocks pores provide negligible permeability but regularly-spaced fractures do provide conduits (Brace, 1980). What is less clear is how and where the transition from porous flow to fracture-controlled flow takes place, given that many crystalline metamorphic rocks started life as sediments. Many sedimentary rocks display dual porosity, with both fractures and pores contributing to their porosity and permeability, and the extent to which fractures develop is related to burial and uplift history.

Perhaps the most important difference between the upper crustal environments in which hydrogeologists and reservoir engineers have developed a sophisticated understanding of how fluids behave, and deeper crustal settings where our understanding is rather poor, is that the nature of the independent variables governing fluid flow may change with geological setting. In shallow settings at low temperatures, such as sedimentary basins, it is reasonable to assign a value to properties such as permeability or porosity to a rock unit, based on its performance in pumping tests and in the laboratory, and treat these as independent variables which will dictate how fluids behave in the formation in response to changes in fluid supply, hydraulic head, etc., but at greater depths and higher temperatures these parameters may themselves become variables (Ingebritsen and Manning, 2010; Ingebritsen and Appold 2012; Yardley, 2009).

In a prograde metamorphic system, pressure loss can trigger further devolatilisation, drawing down temperature as endothermic reactions proceed (Yardley and Cleverley, 2013). Fluid-absent rocks, in which water fugacity is buffered to low values by mineral equilibria, act as sinks for fluid. Free water that penetrates them is rapidly consumed by hydration reactions until the mineral buffering assemblage is completely consumed (Yardley *et al.,* 2010).

Fluid migration in near-hydrostatically pressured sites is very well understood, but the behaviour of fluids in deeper, over-pressured systems has been a source of much controversy amongst metamorphic geologists. *Mike Etheridge* and colleagues (Etheridge *et al.* ,1983, 1984) argued that the near-lithostatic fluid pressures encountered during metamorphism would result in high permeabilities for metamorphic rocks and this would in turn lead to the development of crustal scale convection cells. The difficulty with this model is that the pressure difference between the top and base of a convection cell reflects the density of the fluid, whereas the difference in lithostatic pressure of the host rock reflects the density of the rock. As a result, relative to a point where fluid pressure is equal to rock pressure, fluid pressure decreases less rapidly than rock pressure as you move upwards from the equivalence point, so that the rocks hydrofracture. Similarly, moving downwards, lithostatic pressure increases more rapidly than fluid pressure so that porosity and permeability decrease (see Connolly, 2010, for an elegant and well-illustrated explanation). The vertical extent over which fluid remains connected in a convection cell is unlikely to exceed more than around 100 metres, because rocks undergoing metamorphism are weak. Instead of convecting, metamorphic fluids are likely to move upwards irreversibly. *Jamie*

Connolly has developed ideas about the way in which this happens on a large scale (summarised in Connolly, 2010) and described how, if metamorphic rocks are able to compact as reaction proceeds, fluid will escape in the form of migrating "porosity waves". An important challenge today is integrating this large-scale view with field scale studies (Oliver *et al.*, 1990, 1993; Oliver, 1996; Yardley *et al.*, 1991; McCaig, 1997; Peniston-Dorland and Ferry, 2008).

Connolly's view of metamorphic fluid behaviour makes no unrealistic demands on the crust, but his large scale view envisages that the upper crust, above the region in which metamorphism is occurring, is made up of brittle rocks (*e.g.*, sedimentary rocks) in which fluid pressure is approximately hydrostatic. In contrast, when we trace metamorphosed units to progressively lower metamorphic grades, they often merge into sedimentary sequences that convention would say had experienced diagenesis but not necessarily metamorphism. Slate belts represent some of the lowest grade metamorphic rocks, forming at temperatures that may be well below 300 °C, but far from having deformed in a brittle manner, they provide superb examples of pervasive ductile deformation, largely achieved through pressure solution. At still lower grades, the deeper parts of sedimentary basins contain many examples of fluid pressures substantially exceeding hydrostatic pressure beneath low permeability, clay-rich beds. However, there are some examples of metamorphism occurring beneath a brittle carapace, when older rocks are involved. Upton *et al.* (2003) have produced an elegant synthesis of the geological and geophysical evidence for present-day metamorphic processes beneath the Southern Alps of New Zealand (Fig. 3.7) that provides evidence for fluid escape through brittle crust above a deeper, ductile zone.

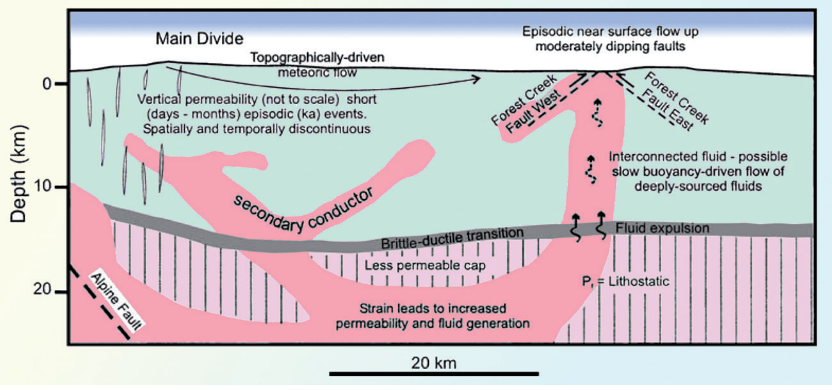


Figure 3.7 An example of large scale behaviour of metamorphic fluids inferred for a remobilised metamorphic belt, southern Alps, New Zealand. Across this section, previously metamorphosed low grade rocks are subject to renewed metamorphism today, with deformation leading to uplift along the Alpine Fault in the west. The upper part of the crust is inferred to behave in a brittle manner with rising fluids episodically interacting with groundwater flow. Below about 15 kilometres, the rocks are inferred to be strongly overpressured due to ongoing dehydration and deformation (modified from Upton *et al.*, 2003).

3.3.1 Veining, flow paths and the roles of infiltration and segregation

Classically, a distinction is made between infiltration metasomatism caused by moving fluids, and diffusion metasomatism for which the fluid is essentially static (Korzhinskii, 1970). Inevitably, diffusion metasomatism is far less significant from the point of view of mass transfer, but it provides useful pointers as to which lithologies become reactive when juxtaposed under metamorphic conditions, and to the assemblages that result. The same general trends will result when, instead of being physically in contact, fluid that has equilibrated with one lithology passes into another lithology due to fluid flow or infiltration. Here, we make a distinction between segregation and infiltration, where segregation refers to any process that concentrates material from adjacent wall rocks into veins or other layers with a distinctive composition, without significant introduction of material from an external source. A simple criterion to distinguish veins formed by segregation from those formed by infiltration is that segregation veins do not normally exhibit metasomatism in their wall rocks, apart from depletion in the minerals that concentrate in the vein, because the fluid phase in the vein remains very close to equilibrium with the host rock assemblage, whereas infiltration of fluids into veins is almost always accompanied by the development of altered vein margins (Richards *et al*., 2002; Yardley, 1986; Yardley and Bottrell, 1992). Thus, in one case (*e.g.*, Figs. 1.3c and 3.8) flow is either very slow or confined within a relatively small and coherent volume, while in the other (*e.g.* Fig. 1.3f) the veins mark paths for infiltration of fluid that is not in local equilibrium (Breeding and Ague, 2002).

Infiltration of fluids into new host rocks can give rise to dramatic metasomatic changes in rock chemistry and is the origin of a wide range of ore deposits. But minerals can also make use of even small amounts of fluid to recrystallise into veins or other cavities via segregation. Such features demonstrate the rock had once contained a free fluid phase, which may also have facilitated physical deformation and played a major role in regional geological development. Whether veins arise from infiltration or segregation has been a long standing source of controversy in the metamorphic community.

An example of the problem is illustrated in Figure 3.8, where a pure andalusite vein in pelite passes into a quartz rich bed and becomes a quartz vein containing only minor andalusite within a few cm of the contact. What both of these veins have in common is that the vein minerals are composed of material that could have been derived from the immediate host bed. Material is redistributed, but not derived from an entirely external source, even though the absence of a depletion halo around the andalusite implies longer transport than would be possible by diffusion alone. Yardley and Bottrell (1992) argued that this is possible if, in the course of syn-metamorphic deformation, schists are embrittled by the high fluid pressure and crack locally, allowing fluid to circulate in the immediate area. Thus transport distances can be greater than could be achieved by diffusion alone, but the fluid is close to equilibrium with the host rocks and veins at all times, so there are no metasomatic effects such as would be expected for infiltration of an exotic fluid.

Of course, no overpressured rock experiencing segregation can be a completely closed system. Some fluid will escape and fluid may be introduced from higher-pressured regions, so segregation and infiltration must be seen as end members. Real veins may have aspects of both.

Figure 3.8 Veined outcrop of schists, Connemara, Ireland, showing a single vein passing from a quartz vein with minor coarse andalusite (A) where it cuts a thin quartzite, to a pure andalusite vein (arrowed) in the adjacent staurolite mica schist. For discussion see text.

3.4 Reaction-Permeability Feedbacks

There are many geological settings in which fluid flow appears to have been focussed through a small rock volume over an extended period of time, resulting in the growth of extensive vein systems or other metasomatic features. In fact, this process is likely required to form the many different types of vein-hosted metal deposits that we mine today. Sometimes continued flow appears to result from continued deformation, thus recracking rocks so that fracture permeability is regularly renewed, and this is probably the most widely invoked cause of metasomatic fluid infiltration. Often, fluid flow results in the precipitation of material from the fluid or the hydration of minerals in the wall rock; this leads to permeability reduction unless deformation and extension continues. However, in some instances, it appears that reactions themselves can create porosity and enhance fluid infiltration. This effect is seen most clearly in marbles and skarns that have undergone decarbonation reactions (Baumgartner *et al.*, 1997).

For example, the reaction:

$$\text{calcite} + \text{quartz} = \text{wollastonite} + CO_2$$

involves a reduction in solid volume of about 33%. If the rock remains rigid through the reaction, this volume change translates into new porosity, and hence enhanced permeability. If porosity collapses as the reaction proceeds, the increase in porosity will be less than this. An example of a wollastonite skarn developed from marble by focussed infiltration is the Valentine wollastonite deposit in the Adirondacks described by Gerdes and Valley (1994). The significance of this feedback between reaction progress and permeability is that the temperature for calcite + quartz to react is much lower if water is introduced to the fluid phase, lowering the CO_2 partial pressure. When no reaction occurs, marbles have very low porosity and permeability; water does not infiltrate and quartz survives to the temperature for reaction with a pure CO_2 fluid. However once the reaction has begun and caused a permeability increase, water from nearby schists may infiltrate the marble, and as it does so the partial pressure of CO_2 is reduced, the reaction becomes progressively overstepped and accelerates. This has the effect of increasing the permeability further, creating a positive feedback (Balashov and Yardley, 1998).

BY writes – The development of wollastonite bands from calcite marbles suggests that feedback does indeed occur when carbonates begin to break down at amphibolites facies temperatures, but is marble really so slow to compact under metamorphic conditions that porosity-creation by reaction can outstrip porosity destruction by creep? I put this question to *Victor Balashov*, who I had met at *Korzhinskii's* old institute – the Institute for Experimental Mineralogy at Chernogolovka, outside Moscow, and he was able to bring together kinetic data for the reaction with information on the creep of calcite to generate a model showing how a quartz-bearing marble adjacent to a rock containing lithostatically-pressured water would develop once reaction began (Balshov and Yardley, 1998; Balashov *et al.*, 1999). As I had expected, a permeable layer developed at the marble edge which provided a focus for fluid flow parallel to the contact, but I was surprised to find that the rate at which the permeable layer migrated into the marble was diffusion controlled, limited by diffusion of water against the flow of carbon dioxide leaving the reaction front.

There is an analogous reaction in dolomitic marbles that produces coarse prismatic diopside. The chemical zonation that arises as infiltrating water introduces Fe means that this reaction results in the most effective petrographic images of reaction-enhanced porosity and permeability (Yardley, 2009; Fig. 3.9).

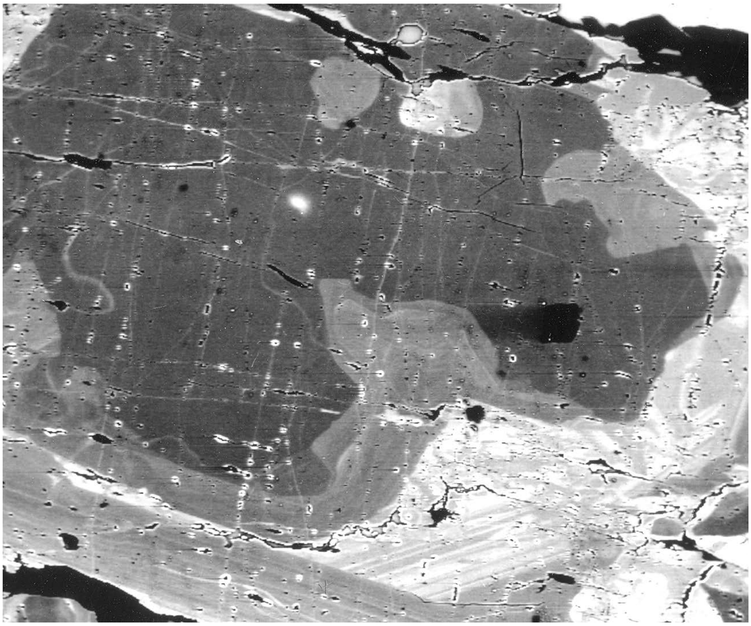


Figure 3.9 Back-Scattered Electron Image of diopside from the skarn illustrated in Fig. 1.2a. The central part of the grain is near end-member diopside (dark grey) and has been corroded and then overgrown by new diopside with a small amount of Fe present (modified from Yardley, 2009).

Yardley *et al*. (1991) argued that the formation of stratabound diopside skarn layers from dolomitic marble created a zone of high permeability, and therefore lowered fluid pressure. Further fluid migrated into the skarn layer from surrounding overpressured rocks and escaped from it at the structurally highest point, where the fluid pressure fractured overlying rocks and formed distinct garnet skarns replacing quartzofeldspathic metasediments (Fig. 3.10). This local flow cell may be a specific example of the type of behaviour that *Connolly* has predicted should occur on a larger scale, although there is no evidence to suggest that the focussed fluid continued to travel as a discrete wave after it had equilibrated with the local psammitic metasediments. Possibly they responded elastically to the surge of overpressured fluid, which was then dissipated through the rock mass. Irrespective of the detailed mechanism, it does seem likely that permeability is dynamic in the metamorphic environment (Ingebritsen and Manning, 2010), and the nature of the relationships was explored in an earlier volume in this series by Jamtveit and Hammer (2012).

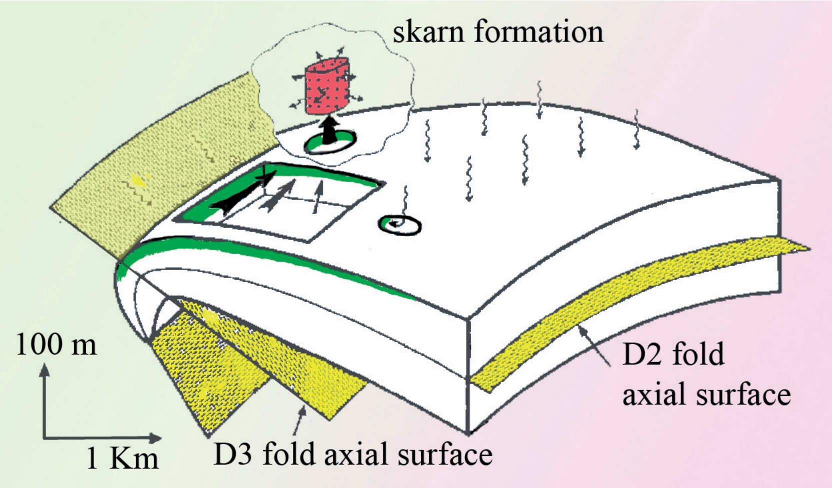


Figure 3.10 Schematic representation of the focussing of metamorphic fluid flow by reactions in marble, leading to skarn-formation. A marble-bearing unit outlines the refolded fold structure and reaction of dolomite + quartz to diopside in the marble has generated secondary porosity, drawing in quartz saturated water from overlying sillimanite schists, and leading to the development of bedded diopside skarn (Fig. 1.2a). Layer-parallel flow in the marble drains the fluid to a structural high point from where it breaks through the overlying schist. Andradite garnet skarn forms irregular crosscutting bodies in these schists and are inferred to complement the bedded skarn (modified from Yardley *et al.*, 1991).

Reaction-enhanced porosity and permeability is particularly well-developed in carbonate rocks, and explains why there is often a sharp transition from thoroughly reacted rocks (skarns) to more or less intact marble, but it seems likely that similar effects can occur in other rocks that experience metasomatism. For example, Tenthorey and Cox (2003) investigated the impact of serpentine-breakdown reactions on permeability.

4. GEOLOGICAL SETTINGS OF CRUSTAL FLUIDS

Thus far, we have emphasised the common features of crustal fluids by discussing them in general terms, but of course the specific fluid compositions and processes may be quite different in different geological settings. One of the main reasons that we are interested in fluids (other than hydrocarbons) is because of what they can do to rocks. Fluids can catalyse mineral reactions, such as the conversion of granulite to eclogite (Austrheim, 1987), change rock strength, focus deformation (Rutter, 1983; Cox, 2010), and change the chemical composition of rocks by adding and removing material in solution, and in extreme circumstances, form ore deposits.

Chemical and mineralogical changes caused by migrating fluids were classically called *metasomatism* by petrologists, but *alteration* by ore deposit geologists. Today, the word metasomatism is used in a way that can embrace a very wide range of scales (see Harlov and Austrheim, 2013).

In the crust, the most extensive metasomatic systems are those that arise at mid-ocean ridges as a result of the convective circulation of seawater, although the metasomatic rocks that result are often destroyed in subduction zones rather than being preserved in the geological record. Other important sources of metasomatic fluids appear to be deep sedimentary basins and cooling plutons. Aqueous fluids from these sources can carry dissolved loads exceeding 25 wt% and can continuously exchange with the wall rock as the fluid:rock system attempts to maintain equilibrium as fluids move. Metasomatic modification of rock compositions by moving fluids *(infiltration metasomatism)* occurs in a wide range of settings, although primarily in the upper crust, where fluid fluxes are largest (Yardley, 2013). Any fluid that moves from one rock type into another with contrasting mineralogy, or simply flows along a single unit to a region with different temperature and pressure, will react with the wall rocks along the way, causing metasomatism.

Most of what we know about fluid processes in the past comes from the chemical changes that they induced in the rocks through which the fluids passed. While metasomatism or "*alteration*" has long been an accepted part of ore deposit research, it has had a much more troubled relationship with petrology in general. Only recently has it emerged as part of the accepted armoury of petrological processes (*e.g.,* Harlov and Austrheim, 2013). In its first heyday in the mid-20th century, metasomatism was viewed by some as a universal panacea whose acid fronts and basic behinds could make any product a geologist might desire from any starting material available. Granitisation, the solid state conversion of country rocks to granite through the action of fluids, was a cornerstone of this incarnation of metasomatism, and while it was an idea that had a reasonable basis in the occurrence of coarse K-feldspar crystals in xenoliths and country rocks around some granites, such observations were extrapolated to take on a regional significance (Valley, 2012). While the metasomatic models of granite formation are now only of historic interest, there is no doubt that they left a legacy of mistrust so that many petrologists were unwilling to consider metasomatism as a viable explanation for any but the most blatant examples of alteration in ore deposits.

The granitisers saw metasomatism as a process that took place in the deep crust and so it is ironic that the rehabilitation of metasomatism began with the discovery of black smoker vents at mid-ocean ridges (Corliss *et al.*, 1979), and the recognition that they vented fluids that had been engaged in metasomatic transformation of the ocean crust at a depth of a few kilometres. In particular, this shallow contemporary metasomatism was recognised as the origin of spilites, albite basalts well-known throughout the geological record, whose origin, whether metasomatic or primary, had been debated for many years (Cann, 1969). Sea floor metasomatism illustrates the range of processes that take place to modify rock and fluid compositions when fluid moves into an environment in which it is not at equilibrium, including both the dissolution and precipitation of components such as $CaSO_4$ or SiO_2 whose solubility increases or decreases in the new environment, and changes in the metal composition of the fluid as some cations are incorporated into minerals while others are released, retaining the charge balance with Cl^-. Where mid-ocean ridge systems differ from many other examples of metasomatism is that seawater is relatively dilute; metasomatic and ore-forming fluids more commonly carry much higher dissolved loads, so that less fluid is needed to produce significant chemical change.

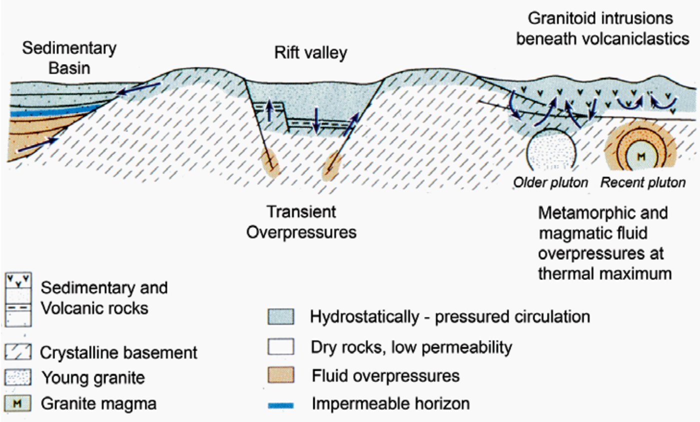


Figure 4.1 Fluid pressure regimes in the upper continental crust. Near the surface both basement rocks and sediments contain hydrostatically-pressured groundwater. At greater depths and higher temperatures, crystalline basement rocks are generally dry except locally where water penetrates during faulting, and here the trapping of water in fissures can even lead to the development of transient overpressures, documented by fluid inclusion densities. Sedimentary basins are hydrostatically-pressured near the surface, but become overpressured beneath seal horizons. Where sediments infill rifts, fluids move from the basin into underlying basement as demonstrated in Figure 3.3, and may also return

> into the basin elsewhere. Where intrusions are emplaced into the sequence at depths of a few kilometres they may emit magmatic fluids and give rise to metamorphic aureoles with near-lithostatically pressured metamorphic fluids. At shallow levels above intrusions, geothermal circulation systems develop in permeable horizons, but these are hydrostatically pressured.

Table 2.1 is a compilation of fluid analyses from a wide range of crustal settings to illustrate the specific accounts of fluid behaviour documented in the remainder of this *Perspectives*. Figure 4.1 is an idealised section illustrating the range of fluid environments expected in crustal settings. The range of fluid processes in magmatic settings are illustrated in more detail in Figure 4.2. Figure 4.1 is drawn up from a physical point of view, to highlight the sites where there is real potential for large scale fluid movement between different settings. Zones of metamorphism contain overpressured fluids, which have the potential to escape into normally pressured regions, while the basal parts of basins contain overpressured fluids that are juxtaposed against an inherently dry basement. Given the right tectonic processes, these are the types of places where focussed fluid fluxes may be generated, but even without such large scale movement all the settings highlighted have a distinctive story to tell about the sorts of fluids they contain and what happens when those fluids move.

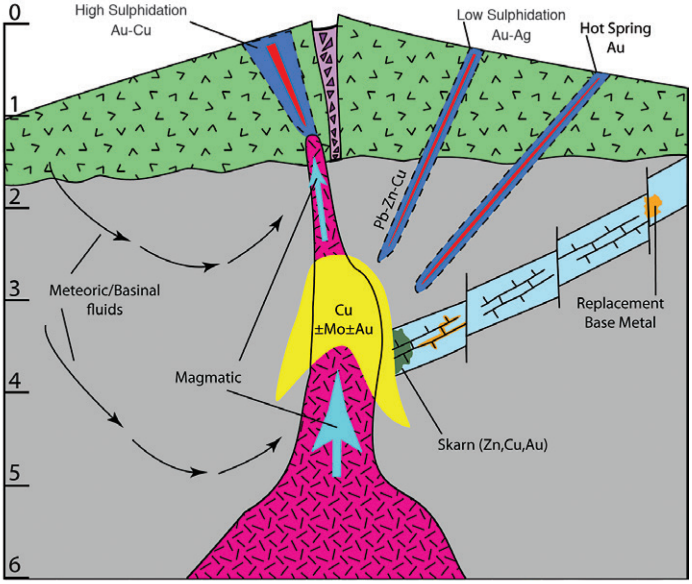


Figure 4.2 Schematic representation of fluid flow associated with epizonal crustal plutons and the associated mineral deposits. Magmatic fluids dominate in the deeper parts of the system where porphyry Cu±Mo±Au mineralisation forms. As magmatic fluids migrate upwards they mix with externally derived meteoric or basinal fluids associated with formation of epithermal deposits.

4.1 Sedimentary Basins

As a result of their high porosity, sedimentary basins provide the largest reservoirs of accessible fluids within the upper crust. They are also the best studied, at least where they are associated with hydrocarbons and base metals. Although basin fill thicknesses may extend to well in excess of 10 km, most of our information about their fluids comes, even today, from depths of less than 2 km. Moreover, recent results from deep basins obtained as a result of commercial drilling for oil and gas are less likely to be published (see however Houston *et al.,* 2011). It is worth bearing in mind that not only does the hydrocarbon industry not take much interest in formation waters, it also does not drill into the hottest, deepest parts of deep basins because most hydrocarbons will not have survived there. This may change in the future with exploration for deep gas. The compositions of formation waters vary greatly between basins, especially where they reside in contrasting geological settings (Houston *et al.,* 2011). They may be highly saline, especially if the sequence hosts evaporites (Rostron *et al.,* 2002; Land and Macpherson, 1992), but are sometimes dilute with a major meteoric component (*e.g.,* the San Juan Basin of Colorado, Snyder *et al.,* 2003). There is also a systematic variation in the salinity of formation waters with depth in most basins that have been studied. Sedimentary formation waters are of significance for much more than just the development of sedimentary basins and their diagenesis because they are often overpressured at depth, and lie above crystalline basement rocks which, we have already noted, are fluid sinks. The importance of formation water interactions with underlying basement rocks for the formation of ore deposits has now been widely recognised (Boiron *et al.,* 2010). It appears likely that they also play a wider role, facilitating deformation and penetrating basement along fractures during extension.

Sedimentary basin fluids are generally, but not invariably, dominated by brines, even in sequences where evaporite beds are not common. Some brines are dominated by NaCl and result from dissolution of halite (Land and Macpherson, 1992), but others are Ca-rich or Br-enriched bittern brines that are residua from halite formation (Rostron *et al.,* 2002; Rittenhouse, 1967; Stueber and Walter, 1991). Sedimentary brines are often mass-limited (see Section 2.1.8) – in other words, the cation load in the pore water has overwhelmed the capacity of feldspars and clays to buffer the relative proportions of Na:K:Ca. This is particularly common where halite beds persist. Where reactive minerals are abundant however, Ca becomes increasingly abundant in more saline fluids, as predicted by equilibrium conditions in Section 2.1.3 (Houston *et al.,* 2011). Figure 4.3 is a flow chart to show the ways in which different pore fluids can evolve depending on the source of the pore water and the minerals with which it can interact.

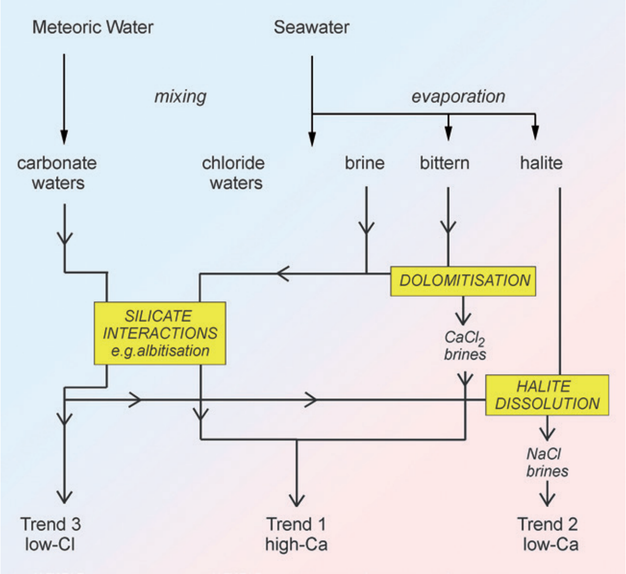


Figure 4.3 Flow chart to show the possible factors determining the evolution of brine chemistry during diagenesis. Initially, meteoric waters give rise to bicarbonate groundwater while seawater can evolve by evaporation to more concentrated brines, or precipitate halite leaving a complementary bittern brine. Meteoric waters may be modified by reaction with minerals but remain as low-Cl waters, whereas highly saline fluids can evolve in different directions. Dolomitisation by bitterns and other brines results in Ca-Cl brines whereas dissolution of halite beds tends to lead to low-Ca, Na-Cl brines (after Houston *et al.*, 2011).

It is a fascinating and counterintuitive observation that bittern brines are widespread in the subsurface even though we rarely see halite beds forming and such beds are often scarce in sequences hosting bittern brines. Presumably, this is because the brine from which halite beds precipitate has a greater chance of being preserved in the geological record than the solid halite beds themselves. This is not surprising, since the brine is dense and will sink through the sediment column displacing less saline pore waters, whereas the "rock" readily dissolves as a result of climate or sea level changes, or by extreme events such as a tsunami. Evolved bittern brines are enriched in Mg and K, and there is widespread evidence for their involvement in dolomitisation of limestones (often associated with base metal mineralisation (*e.g.,* Kesler *et al.,* 1995). The high K/Na ratios attained in evolved bitterns (Fig. 2.12) preclude equilibration with Na-feldspars and may drive K-feldspathisation; more commonly, basinal brines have lower K/Na ratios, close to albite – K-feldspar equilibrium values, or are strongly Na-enriched due to halite dissolution (Fig. 2.12).

In some basins, the fluids now present may not be closely related to the original sediment pore waters. In the North Sea region, there is widespread evidence of meteoric water flushing of the porosity, which had a major impact on the diagenetic evolution (Glasmann *et al.*,1989; Walderhaug and Bjørkum, 1992; Wilkinson *et al.*, 1994). In North Germany however, formation waters below the Zechstein evaporates were not replaced by subsequent flushing (Lüders *et al.*, 2010). Pore waters of the Cretaceous Fruitland Formation from the San Juan basin of Colorado likewise show evidence of meteoric water flushing in the vicinity of surface outcrops, but otherwise do not appear to have changed significantly since diagenesis (Snyder *et al.,* 2003).

There has been considerable controversy over the past 25 years concerning what controls formation water chemistry in basins. The first issue is the extent to which fluid compositions reflect chemical equilibrium as opposed to responding only to the fastest reacting phases. Looked at from the perspective of newly deposited sediments, it is clear that early diagenetic changes will be dictated to a significant degree by kinetics (Coleman *et al.*, 1985), but when the chemical composition of mature formation waters has been evaluated, there is equally good evidence that it is in equilibrium with the host minerals (Hanor, 1994). These chemical controls are considered in more detail below. Separately, there is a growing body of evidence that seawater composition has changed over geological time (Hardie, 1996). The extent to which this temporal variation may influence formation waters is however controversial. Lowenstein and Timofeeff (2008) claimed to see a parallel change in formation waters, but on the face of it this contradicts the evidence for mineral buffering of formation water chemistry.

Another important characteristic of sedimentary formation waters is that they decrease in abundance with depth. Empirical relationships have been proposed to link depth and porosity, but of course local geological controls will always be a major consideration. Porosities decline with depth through a combination of compaction and diagenesis. In the case of clay-rich rocks, compaction and expulsion of pore waters probably plays a major role, whereas for sandstones, infilling of pores by mineralogical reactions is probably more important (Magara, 1980). Exceptions to the general trend of decreasing porosity with depth are often associated with elevated pore pressures.

4.1.1 Ore deposition in sedimentary basins

Among the best-known and most-studied mineral deposits occurring in sedimentary basins in continental settings are the Mississippi Valley-Type Pb-Zn-Ba-F deposits (MVTs). MVTs are epigenetic, stratabound deposits hosted dominantly in carbonate rocks and mostly of Phanerozoic age (Leach and Sangster, 1993; Leach *et al.*, 2005). The fluid environment in which MVT deposits form is thought to be analogous to that which exists today in petroleum basins, with many similarities between modern basinal (oilfield) brines and MVT mineralising fluids (Carpenter *et al.*, 1974). The link between saline evaporite fluids and many sedimentary ore deposits is also well established (Warren, 1997). Moreover, considerable geochemical and geologic evidence has been presented documenting the migration of mineralising fluids over long distances (10s to 100s of km) in response to collisional tectonics which drive the fluids basinward from the foreland fold and thrust belts (Leach and Rowan, 1986).

Many of the earliest fluid inclusion studies of ore deposits focused on MVT deposits, owing to the relatively large size of the inclusions and their low homogenisation temperatures. These two factors made it possible to acquire quantitative microthermometric data despite the crude heating and cooling stages and the poor quality optical microscopes (compared to modern instruments) available a half century ago (*c.f.*, Bailey and Cameron, 1951; Newhouse, 1933; Roedder, 1967, 1968, 1971b, 1977, 1979). In recent years, Basuki and Spooner (2002), Wilkinson (2001) and Bodnar *et al.* (2014) have summarised data obtained from fluid inclusion studies of MVT and similar deposits.

Sedimentary basins can reach 10-15 km in thickness and probably approach temperatures of lower greenschist metamorphism at these depths. Most MVT deposits are thought to form at temperatures less than about 200 °C, suggesting maximum depths of less than about 6 km. Stable isotopic studies (D/H and $\delta^{18}O$) of waters from sedimentary basins reflect the results of water-rock interaction during basin subsidence and diagenesis. Most basinal brines show isotopic compositions that lie along linear trends that extend either from the local meteoric water line (or from seawater) to higher $\delta^{18}O$ values (Fig. 2.13), reflecting the exchange of oxygen in water (relatively low $\delta^{18}O$) with oxygen in the rock (relatively high $\delta^{18}O$) as described above.

Bodnar *et al.* (2014) compiled homogenisation temperatures (Th) of fluid inclusions in sphalerite, which is one of the major ore minerals in MVTs, for 38 MVT deposits. The total range in Th observed, which varies from about 75-200 °C, is comparable to the range observed for other minerals in all MVT deposits and is consistent with formation at depths of ~2-6 km.

Compositions of fluids in MVT deposits have been constrained by two different but related sources of information. It is generally accepted that MVT deposits form from fluids that are identical to basinal brines produced during the drilling into continental sedimentary basins. Carpenter *et al.* (1974) were among the first to analyse and compile compositions of basinal brines, and Collins (1975) complied compositions of oilfield brines from around the world and related compositions to age, rock type, and other physical and geological properties. The common feature of these and many other studies of basinal brines is that they are mostly dominated by Ca and Na chlorides. Potassium is generally low as K is sequestered in clay minerals during diagenesis, but there are exceptions where the initial fluid is a highly evolved K-rich bittern brine as noted above.

Compositions observed in basinal brines are comparable to those determined for fluid inclusions in MVT deposits. For example, Hall and Friedman (1963) extracted and analysed fluid from inclusions from the Cave in Rock fluorite district and from the Upper Mississippi Valley MVT district by crushing fluid inclusion bearing minerals in distilled water. They found that the fluids were dominated by Na and Ca chlorides, although the ratio varied depending on the host phase and location. It should be noted that this work was among the earliest fluid inclusion analyses to be conducted, and the authors were not aware of the many problems associated with extracting fluids from inclusions by crushing, especially the sorption of divalent cations onto the newly-formed and negatively-charged mineral surfaces, as described by Bottrell *et al.* (1988). Kesler *et al.* (1995) demonstrated that different MVT deposits in the USA included both districts in which the ore fluid was an evolved bittern brine and others in which it was a halite dissolution brine.

Subsequently, Haynes and Kesler (1987) analysed fluid inclusions from the Pine Point, Northwest Territories, Canada, and the East Tennessee district MVT deposits by heating the inclusions until they decrepitated (exploded) and then analysing the decrepitates (solid precipitates) using SEM-EDS. All compositions fell along the $NaCl$-$CaCl_2$ join, and potassium concentrations were very low in all inclusions, similar to what is observed in basinal brines.

RJB writes – When Haynes and Kesler presented their preliminary results at a conference in the mid-1980s, I was in the audience and was rather sceptical of the results. It seemed to me that the decrepitation method was too random and unpredictable to give reliable results. As Fred Haynes was a friend and we had been fellow graduate students together at the University of Arizona before Fred went off to work with Steve Kesler at the University of Michigan while I went to Penn State via the USGS, we talked about his study over a beer and decided to do a collaborative follow-up study using the technique that Mike Sterner and I had recently developed to produce synthetic fluid inclusions of known composition. So, Mike and I prepared synthetic fluid inclusions with known Na/Ca/K ratios and shipped these off to Fred to analyse – without, of course, telling him what the compositions were. Fred did the analyses, and with only some minor differences that were later fixed by slightly modifying the technique, obtained the correct and known cation ratios. This was a classic example of a technique (synthetic fluid inclusions) looking for a problem to tackle (development and confirmation of an analytical protocol). It is unfortunate that in today's funding climate if a researcher submits a proposal to develop a methodology, funding is often declined because the research is not hypothesis-driven. Yet, it is often these methods and techniques that, once developed, help to solve important problems and advance science.

In recent years, individual fluid inclusions from the Tri-State and Northern Arkansas MVT districts in the North American mid-continent were analysed by laser ablation ICPMS. Wenz *et al.* (2012) reported Na/Ca values associated with sulphide mineralisation that were lower than values from fluid inclusions (FIs) in gangue minerals. This is the same trend that was reported by Haynes and Kesler (1987) for the Pine Point and East Tennessee MVT deposits, where sphalerite FIs have the lowest Na/Ca ratios of all minerals studied. A similar trend in Ca/Na ratios was observed in the Silesia-Cracow MVT deposits, eastern Europe. Leach *et al.* (1996) report that the fluid Ca/Na is controlled by dolomitisation, whereas Wenz *et al.* (2012) attributed trends in Ca/Na in the Tri-State and Northern Arkansas districts to fluid mixing.

Similar to what has been noted for the major element compositions of MVT fluids, abundant data are available on the metal contents of basinal brines because they are encountered through drilling during petroleum and natural gas exploration and production. Carpenter *et al.* (1974) reported Pb concentrations up to 111 ppm and Zn values up to 575 ppm in oilfield brines from the U.S. Gulf coast region. Yardley (2005) and Houston *et al.* (2011) presented more recent compilations of metal concentrations in a wide range of geologic environments and reported Pb and Zn concentrations up to about 100 ppm and to several hundred ppm, respectively, in basinal brines and MVT deposits. Yardley (2005) showed a strong correlation between Zn and temperature across all crustal brines, and the Zn concentrations from Carpenter *et al.* (1974) are higher than would be expected from the temperatures recorded in the wells. This might reflect changes in the temperatures of the brines through time, since the levels are not limited by zinc chloride saturation.

Among the first reports of concentrations of metal in FIs from MVT deposits was by Pinckney and Haffty (1970) for the Cave in Rock district, southern Illinois. These workers crushed FI-bearing quartz, fluorite and barite under vacuum and analysed the fluids by atomic absorption spectroscopy and found up to 1040 ppm Zn and up to 350 ppm Cu. Metal concentrations decreased from early to late stages.

While laser ablation ICPMS has been applied successfully to analyse FIs from a wide range of ore deposit types, it is not without its limitations, and these are perhaps best illustrated in the MVT deposits. In many deposits, the most abundant gangue mineral is quartz and, therefore, contamination of the FI signal by the host has little effect on the concentrations of the elements of interest. Conversely, in the MVT deposits, quartz is relatively uncommon and when present is generally not associated with the sulphide mineralisation. The most common gangue minerals are carbonates (calcite, dolomite and sometimes ankerite), with lesser amounts of barite. And, while major elements in the ore fluid can be determined directly by analysing FI in the ore mineral sphalerite, host contamination is a problem when analysing for metals, including Zn, Cu, Fe, and Cd. Most workers who have measured metals in FIs in sphalerite have focused on Pb, which is assumed not to be incorporated into the sphalerite structure. Thus, Stoffell *et al.* (2008) report Pb concentrations of 1.3-18.3 ppm in FIs from the Tri-State district, and 0.83-98.6 in FIs from the Northern Arkansas district, with the highest values for FI in sphalerite. Zn concentrations in FIs in quartz and calcite from the two districts ranged from 2.82-11.5 ppm, but it is unclear how these values relate to the fluids associated with sulphide mineralisation.

Wilkinson *et al.* (2009) analysed FIs in sphalerite from the Northern Arkansas district of the Ozark Plateau, North America, and from the Midlands Basin orefield in Ireland. [Note that there is some debate as to whether the

Irish deposits should be considered MVT deposits, since they appear to have formed below the sea bed while sedimentation was still proceeding (Wilkinson *et al.,* 2009)]. These workers reported low Zn concentrations in FIs in the gangue mineral quartz (all but one below detection in the Irish deposits). They also determined the Pb content of FIs in sphalerite (they could not analyse for Zn owing to contamination from the host), and used the measured, constant ratio between Zn and Pb concentrations of FIs in quartz to calculate the Zn content of FIs in sphalerite and obtained concentrations of 3,000 to 5,000 ppm in the fluid inclusions. These concentrations are up to two orders of magnitude higher than for fluid inclusions in presumably coeval carbonate and silicate gangue minerals. These results document the importance of NOT assuming that compositions of FIs in gangue minerals that are texturally in equilibrium with sulphides are the same composition as FIs in the sulphides. Wilkinson *et al.,* (2009) conclude that, even when there is clear petrographic evidence that the gangue and ore minerals are coeval, FIs in the gangue minerals may not contain the ore-forming fluid.

4.2 Metamorphic Fluids

Despite being studied by almost completely different groups of Earth Scientists, *i.e.* sedimentary petrologists and petroleum geochemists versus metamorphic petrologists, there is actually no clear distinction between fluids in sedimentary basins and those found in sediments undergoing prograde metamorphism. Instead, there is a continuous evolution from sedimentary basin to high grade metamorphic fluids. Nevertheless, despite originating as sedimentary formation waters, metamorphic fluids present a series of distinct challenges that makes them quite unique. In the first place, their chemistry can exhibit large variations in both solvent and solute composition, although the two are inextricably linked through the phase relationships and are related to the protolith being metamorphosed. Thus, the chemical potentials of the solvent species, generally simplified to H_2O and CO_2, are controlled by mineral equilibria, whereas the dissolved load is dictated by chloride content. Whether a mixed volatile, $H_2O - CO_2$ fluid forms a single phase or two immiscible fluids depends on the chloride concentration as well as on temperature and pressure, as we have discussed in detail in Section 2. Metamorphic fluids are certainly less abundant than basinal fluids, but they have evolved from sedimentary fluids through continuous exchange and re-equilibration (Yardley, 2009).

BY writes – I first appreciated just how close sedimentary and metamorphic rocks can be when I was taken by *Doug Coombs* on an Otago University field class to the southernmost part of the South Island of New Zealand, to visit some of the classic examples of burial metamorphism that he first described in the 1950's (Coombs, 1954). Conditions were not good. *Coombs* responded to the hail storms that blasted us on one beach by drawing ever more complex phase diagrams in the sand with a stick- the hailstones filled the lines beautifully and made them easier to see. When it came to the examples of burial metamorphism however, what struck me was the similarity of the shale interbeds between the zeolite-bearing greywackes to the shales that I had been shown as a student in Mesozoic basin sequences of the UK. I realised that what was different between Southland and the margins of the North Sea was that in one case the sandstone beds were greywackes composed of igneous material, including abundant glass, which reacted strongly with water to produce distinctive zeolite minerals, while in the other the sandstones were clean quartz sands with minor alkali feldspar, having much less potential to take part in low grade reactions. The physical environments were comparable, but the sediment very different. This observation made me begin to think of metamorphic and sedimentary rocks as part of a continuum, especially when it comes to the fluid phase.

There is a common perception that metamorphic fluids have compositions along the H_2O – CO_2 binary, and that their dissolved salt content is negligible. This is based in large part on the systematic study of fluid inclusions from the western Alps by Mullis *et al.* (1994) that showed systematic variations in fluid composition with metamorphic grade. This conclusion was based primarily on data from fluid inclusions in late-stage veins rather than peak metamorphic samples, for the simple reason that peak metamorphic fluids are rarely preserved. Wider compilations of metamorphic fluid compositions reveal a pattern that is much closer to sedimentary basin fluids. Yardley and Graham (2002) reported a very wide range of published salinities, and while the low salinity fluid inclusions commonly contain visible CO_2, the more saline ones do not, in accord with the phase diagram (Fig. 1.1). Their compilation showed that metamorphic fluids from sequences deposited in continental shelf settings were commonly very saline, even at high grades, while those from accretionary and oceanic settings were much less saline (Fig. 2.8). An example of how prograde metamorphic fluids evolve from basin brines by continuing cation exchange and release (occasionally incorporation) of water or gases is provided by the low-grade metamorphic fluids in the emerald-bearing veins from Colombia (Banks *et al.,* 2000). These have Br-poor signatures typical of basinal brines derived from halite dissolution, but show more evidence of cation exchange with their host rocks compared to most basinal fluids (Yardley, 2013; Fig. 4.4), for example they are much richer in Ca than sedimentary brines with comparable Br/Cl ratios. This is not a surprising result in view of the presence of evaporites in the region and the relatively high temperature of formation of the emerald veins.

The cation chemistry of metamorphic fluids follows the rules outlined in Section 2 and there are a limited number of experimental studies that provide calibrations. The general principal that the ratio of divalent cations to monovalent cations will increase with increasing chlorinity, outlined in Section 2.1.3, still holds true. For Ca, an additional factor is that, although plagioclase equilibria control Na:Ca relationships at high grades (see Section 2.1), at low grades, Ca-plagioclase is unstable and relatively soluble Ca-minerals such as epidote occur instead. For almost all possible redox environments, Fe and Mn will be much more abundant than Mg in the fluid phase, while K concentrations are invariably lower than those of Na, but the K:Na ratio increases progressively with temperature.

Si concentrations are almost certainly controlled by equilibrium with quartz. Figure 2.7 shows the levels to be expected if the fluid is pure water, although modest concentrations of dissolved salts have little effect (see Section 2). Dissolved CO_2 or very high salt concentrations lower the activity of water in the fluid (see Section 3.2.1) and so inhibit the formation of solvated aqueous silica. An interesting consequence of this effect is that if CO_2-bearing fluids exsolve gas due to pressure drop, then they become silica undersaturated and will dissolve additional quartz. Much less is known about the solubility of the other major rock-forming component, Al. It has been widely assumed that Al concentrations in metamorphic fluids are extremely low, because this is clearly the case in the $Al_2O_3 - H_2O$ system (Manning, 2006; Newton and Manning, 2008). However the abundance of Al-minerals such as feldspar, tourmaline and of course the Al-silicate polymorphs in veins formed over a wide range of metamorphic conditions suggests that there must be sufficient levels of Al in solution to permit significant segregation. This discrepancy has been resolved by the work of Manning (2006) and Newton and Manning (2008) who have demonstrated that, although the solubility of pure corundum is low, Al-silicates have higher solubilities and these are further enhanced if the fluid is a brine. These observations are interpreted as the result of formation of Al-Si and Al-Si-Na aqueous complexes, and they are a further demonstration that when it comes to experimental fluid studies the classic experimental approach of working with idealised pure end-member systems can sometimes fail to capture what is important in nature. It is possible that other common ligands, such as borate or fluoride, may further enhance Al-solubility, but to date experimental data are largely lacking.

When we discuss metamorphic fluids, we are implicitly concerned with the production of fluid by metamorphic reactions, and the bulk fluid evolution as it is depleted by flow (an inevitable consequence of its low density and overpressure, Connolly, 2010) and replenished by mineral breakdown. However metamorphic fluids are transient as we discussed earlier: metamorphic rocks contain fluids while they are undergoing active metamorphism, either prograde or retrograde, but this fluid does not persist except as isolated inclusions. This is in marked contrast to sedimentary basins, where original pore waters persist for geological periods of time.

Active prograde metamorphism provides a setting in which fluids can occur in chemical equilibrium with deep crustal rocks, and is the subject of most work on deep fluids. Most emphasis today is on subduction zones; these are the settings we can image today. Indeed, geophysical methods are able to image fluid-rich zones under favourable conditions (Wannamaker *et al.,* 2002; Brown *et al.,* 2005). The geological record of orogenic belts gives a rather different picture of where metamorphism occurs, almost certainly one that is skewed by the fact that subduction zone metamorphism is all too often followed by melting, foundering or assimilation into the mantle, whereas the final stages of metamorphism in an

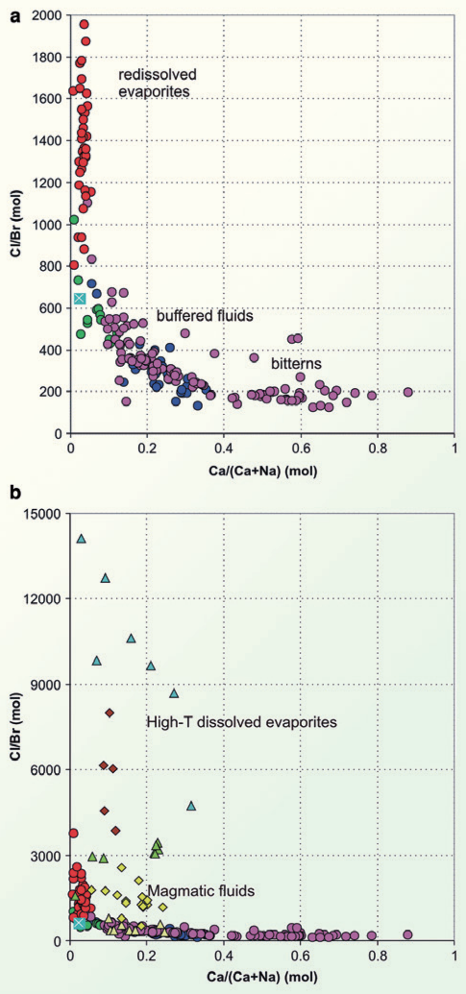


Figure 4.4 Relationships between the proportion of Ca to Na in crustal brines and the origins of their salinity, as indicated by Cl/Br ratios. Part **(a)** shows sedimentary brines and demonstrates a strong correlation between the origin of brines as either bitterns derived by evaporation beyond the onset of halite precipitation, or products of dissolution of halite, and the proportion of Ca to Na in solution. Part **(b)** shows the data set extended to include high-T fluids. Magmatic fluids (diamond symbols) do not show extreme values for the most part (exceptions are linked to magma emplacement through evaporites, Campbell *et al.*, 1995). Metamorphic fluids (triangle symbols) associated with halite retain distinctive high Cl/Br ratios but contain higher levels of Ca than sedimentary redissolved evaporites brines, probably reflecting more extensive fluid-rock interaction (after Yardley, 2013).

orogenic cycle are far more likely to be preserved. While eclogites are proving to be remarkably widespread, many of the old metamorphic rocks that we see at the surface today never experienced subduction, for example metamorphic rocks associated with arc or back-arc settings typically underwent only limited subduction followed by heating during uplift. These settings appear to be much less important at any instant in time than subduction settings, but the preservation potential of Barrovian assemblages, marking the return to an average crustal thermal gradient, is evidently high.

An inevitable consequence of having elevated fluid pressure in metamorphic rocks (*i.e.* greater than hydrostatic pressure) is that fluid cannot recirculate or convect, it can only leak away towards areas of lower hydraulic head (see Section 3.3). Most likely, this means overlying rocks, but in fact if permeable pathways are developed in the metamorphic pile, for whatever reason, they will suck in overpressured fluid from all directions, above and below. This situation contrasts markedly with the conditions prevailing near the surface where extensive fluid circulation can take place, and it means that models for fluid flow and mineralisation in the upper crust cannot simply be extrapolated to metamorphic systems.

Overall, metamorphism is driven by the introduction of heat (which dictates how fast endothermic reactions can take place to release fluid), and hence the overall rate at which water can be driven off from minerals is linked to the rate of heat supply. To maintain fluid pressure near lithostatic pressure, the permeability of the rock must allow fluid to leave the rock at the same rate that it is generated. If the rock is any more permeable, fluid pressure will drop below lithostatic; if less so, overpressure will build up causing an increase in permeability through an elastic response or through hydrofracturing. Based on crustal heat flow values the permeability of rocks undergoing rapid metamorphism in a thermal aureole has been estimated at around $10^{-19}m^2$ (Yardley, 1986; Hanson, 1992), while regional metamorphism is likely to generate permeabilities perhaps an order of magnitude smaller. These estimates are broadly comparable to values proposed by Manning and Ingebritsen (1999) that were, however, not constrained by the need to maintain fluid overpressures in rocks undergoing metamorphism. The subject of metamorphic "hydrology" remains controversial and poorly-understood. Many attempts to estimate fluid fluxes accompanying metamorphism do not recognise the strictly limited amount of fluid available as a constraint, and yield very large estimates that are inconsistent with the fluid being overpressured and therefore unable to recirculate (see discussion in Yardley, 2009). And yet the phase equilibrium calculations used in the estimations of fluid flux are based on the assumption that fluid pressure is equal to lithostatic pressure, which requires very low permeabilities!

4.2.1 Orogenic gold deposits

Gold deposits hosted in metamorphic rocks are widely referred to as orogenic gold deposits and these include some of the largest gold deposits outside the Witwatersrand basin. The simplest "orogenic gold" deposits are quartz vein systems, hosted by low-grade metamorphic rocks and formed during uplift after the main episodes of regional ductile deformation. However, larger deposits are typically more complex and are associated with deep crustal fault zones and form over a depth range of ~2-20 km (Goldfarb *et al.*, 2005). At present a wide range of deposits hosted by metamorphic rocks are included under the "orogenic gold" heading, including some that are almost certainly related in part to igneous activity (Yardley and Cleverley, 2013).

Unlike some other ore deposit types about which the fluids have been identified from direct sampling of modern, active systems, it is not possible to sample fluids from actively-forming orogenic gold systems, but there is an extensive literature on their fluid inclusions. It should be emphasised, however, that considerable uncertainty exists as to whether the inclusions being studied are associated with mineralisation. The earliest known study of fluid inclusions in an orogenic gold deposit is by Königsberger, who studied fluid inclusions from alpine gold-quartz veins in Switzerland (Königsberger, 1901; Königsberger and Müller, 1906). Remarkably, these workers recognised that the fluid inclusions contained low salinity H_2O-CO_2 fluids. Later, Ferguson and Gannett (1932) identified two populations of inclusions in quartz from the California orogenic gold deposits. One type occurred in quartz cores and the other occurred along trails that crosscut individual quartz crystals. Today, we know that in many deposits the secondary fluid inclusion assemblages along trails are the ones most closely associated with gold mineralisation. Modern studies confirm the ubiquitous occurrence of low salinity H_2O-CO_2 fluids associated with orogenic gold systems, and in some deposits large and uniform inclusions occur that have permitted extensive analytical studies. The Brusson district of northern Italy has some of the best studied examples (Diamond, 1990; Yardley *et al.*, 1993; Pettke *et al.,* 1999) although it is worth noting that the gold production from this district has been rather minor. For a detailed summary of the compositions and PT conditions associated with orogenic gold deposits, the reader is referred to our recent publications (Bodnar *et al.,* 2014 and Yardley and Cleverley, 2013).

If the heat flow constraint on metamorphism is always valid, then metamorphic fluids can only be generated slowly, except perhaps locally in response to significant overstepping of specific reactions. Despite this, many geologists have described examples of "orogenic" gold-quartz veins that appear to be linked to the migration of metamorphic fluids but also appear to have been formed very rapidly.

For many years, one of us (BY) was completely mystified by the problem of reconciling the slow rate of heat input to drive metamorphism with the fast rate of formation of gold deposits apparently linked to metamorphic fluids. The penny finally dropped in the light of integrated petrology and geochronology carried out by Craw *et al.* (2010) on mineralisation in Taiwan. This study demonstrated that the gold-quartz veins formed during rapid uplift at the end of the metamorphic cycle. Under low to medium grade P-T conditions, the slopes of many metamorphic dehydration reactions appear as diagonals on a P-T diagram, meaning that they can be crossed during rapid uplift as well as by heating. In this case, the endothermic devolatilisation reactions lower the rock's temperature as they progress, but as long as pressure continues to drop, the reaction will continue and the P-T conditions of the rock mass will track the equilibrium curve of the reaction (Yardley and Cleverley, 2013; Fig. 4.5). Furthermore, if rocks undergo dehydration due to uplift and erosion and fluid pressure approaches lithostatic pressure, then the continuing pressure reduction will promote hydrofracturing and the focussed metamorphic fluid flow along cracks (*c.f.,* Weatherley and Henley, 2013).

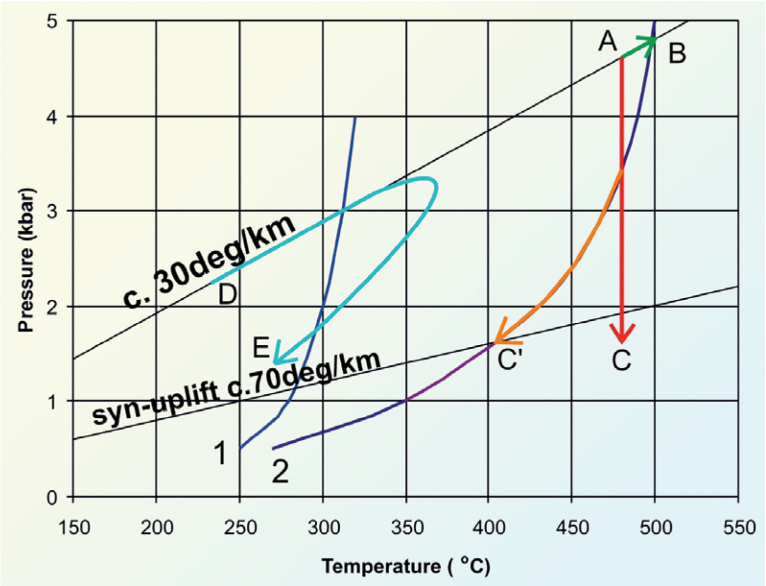


Figure 4.5 The possible effects of rapid uplift of low to medium grade metamorphic rocks on their continuing evolution. Curves 1 and 2 are representative dehydration equilibria. Path A-B shows the change in P-T conditions to be expected in a period of 4 Ma for heating at 10 °/Ma along an average crustal geothermal gradient, whereas A-C shows the effect of 4 Ma of uplift at 2.5 mm/a with no heat loss or reaction. Path A-C' shows the effect of dehydration occurring as a result of uplift, with release of c. 5% H_2O driving a drop in temperature. Path D-E is shown for reference and demonstrates how slow uplift accompanied by cooling leads to retrograde rather than prograde reactions (after Yardley and Cleverley, 2013).

It is still not clear how widespread uplift metamorphism is in nature. In the amphibolite facies for example, many dehydration reactions have very steep P-T slopes and are hard to cross as a result of erosion. Nevertheless, *Linc Hollister, Page Chamberlain* and their colleagues have been advocating the importance of metamorphism during decompression for some time, and it seems clear that it extends far beyond the formation of gold deposits (Winslow *et al.*,1994; Davidson *et al.,* 1997).

4.3 Crystalline Basement

By "crystalline basement" we mean metamorphic and igneous rocks that are at a lower temperature than at the time of their original formation – most of the thickness of the continental crust away from areas of active orogenesis, extension or magmatism is probably in this condition. The significance of this definition, which is developed further below, is that the onset of cooling results in the remaining metamorphic fluid present in pores being consumed by retrograde reactions so that the rock lacks a pervasive pore fluid. Crystalline basement rocks are typically extremely impermeable, at least at the hand specimen scale, and therefore are often assumed to be lacking in fluid, or at least to be of very minor significance as reservoirs relative to adjacent sedimentary rocks. At a larger scale however, crystalline rocks in the upper crust are often fractured and have significant permeability as a result. We have already seen that water is not stable over the long term in most crystalline rocks of the upper crust, being consumed to form hydrous retrograde minerals. However, crystalline rocks invariably contain joints and fracture zones defined by retrograde alteration of primary assemblages and often by precipitation of secondary minerals. Thus, water does reside in crystalline rocks at times, and where fracture walls are completely altered or coated it may remain stable for extended periods. In some situations, such as during active faulting and extension, crystalline rocks may be repeatedly fractured and infiltrated by water from surface or basinal sources. The evidence of deep basement hosted aqueous fluids from deep drilling (notably at the KTB site, Möller *et al.*, 1997; Grawinkela and Stöckhert, 1997), from shield brines (Fritz and Frape, 1987) and from fluid inclusion studies suggests that beyond the reach of shallow circulation systems they are typically very saline and the $CaCl_2$ to NaCl ratio increases with increasing depth (and temperature), probably reflecting the breakdown of plagioclase under conditions where albite remains stable.

Crystalline basement rocks are not a fluid source. In general they provide a sink through hydration reactions, but they are sufficiently reactive to water that they are able to impose a distinctive chemical signature on fluids that infiltrate them. Basement-fluid interactions have been implicated in the genesis of a number of important types of ore bodies, including both those hosted in the basement and those developed in overlying sedimentary formations. For example, while Mississippi Valley-Type (MVT) deposits occur mostly in carbonate rocks in Paleozoic basins, Pb isotope data suggest that at least some of the metal is sourced in underlying granitic basement rocks (Leach *et al.*, 2005). Similarly, the Athabasca-type (unconformity-associated) uranium deposits usually occur at the unconformity between overlying meta-sediments and underlying gneissic basement (Jefferson *et al.*, 2007). Coupled fluid flow / water-rock interaction models suggest that the deposits formed as oxygenated fluids migrated through sandstone aquifers and transported uranium in the oxidised state (U^{+6}), and deposited uraninite at the interface between the sandstones and underlying graphitic metamorphic basement as uranium was reduced to U^{+4} (Raffensperger and Garven, 1995). This interpretation is supported by analyses of fluid inclusions from deposits in the Athabasca Basin that show significantly elevated uranium concentrations in the brines (Richard *et al.,* 2012).

The direct evidence for aqueous fluids in crystalline basement rocks is somewhat sparse, but deep drilling in the Kola peninsula first found deep inflows, while more fully instrumented drilling at the KTB (Kontinentales Tiefbohrprogramm der Bundesrepublik Deutschland) site in Germany reported saline fluid inflows to the borehole from fractures in metamorphic rocks at depths of over 6 km (Möller *et al.,* 1997). Fluid-filled fractures appear to be lined with retrograde alteration products indicating that the wall rocks have reacted with deep brines. When the KTB system was first drilled, the electrical connection was by graphite-lined faults, confirming that the fluid-filled fractures were isolated (ELEKTB, 1997). These observations are consistent with field observations of crystalline rocks. Retrograde alteration is actually widespread (*e.g.,* Holness, 2003; see Yardley *et al.,* 2014) but is much more common in the field than in the teaching laboratory because of the obsession of generations of petrologists to trim off "altered" material from the edges of their specimens before carrying them home. [Note that this is the opposite of what ore deposit geologists do – they carry home only the altered and mineralised rocks!] That "rock-trimming" can be done to such great effect as to mislead generations of geologists is testament to the fact that, as in the KTB hole, fluid that penetrates crystalline rocks does so along fractures, not through porosity (which is virtually non-existent), and so large volumes of rock that almost preserve their peak-T assemblages are transected by narrow zones of retrograde alteration marking former fluid pathways that operated, perhaps only briefly, during crustal residence and uplift. At higher temperatures, the infiltration of water into crystalline rocks is intimately associated with the development of retrograde shear zones (McCaig, 1997). The presence of water in crystalline rocks at greenschist facies temperatures makes them much weaker than the dry rock (Rutter, 1983) and so strain is partitioned into the hydrated regions. Most examples of retrograde shear zones form under greenschist facies conditions, but higher temperature examples are known. As with fluid-filled fractures in the cooler upper crust, water cannot survive indefinitely in high-grade rocks, except in isolated pockets where it is enclosed entirely by low-T hydrated assemblages that isolate it from remnant high-grade assemblages. Hence, we can think of cooled crystalline rocks at all levels of the crust as essentially dry but locally containing transient fluid-filled fractures from time to time. This petrological view of a dry, strong deep continental crust (Yardley and Valley, 1997) is increasingly supported by geophysical data (Jackson *et al*., 2008).

BY writes – It was a matter of luck that I was first introduced to retrograde metamorphism through an outstanding field example. During the long hot summer of 1976 I returned from a Harkness Fellowship at the University of Washington and got a temporary job with the Irish Geological Survey as assistant to *Barry Long* and *Michael Max,* mapping metamorphic rocks broadly similar to those I had studied for my PhD, but in the rolling bogs of the Ox Mountains, inland County Mayo. I had no car and so for transport in the field I was supplied with an official bicycle (illustrated in the Introduction). This meant a trip to the Post Office Stores in Dublin, where vast stocks of increasingly obsolete black bicycles were stacked in serried ranks. These had been built to last: there was just the one gear so nothing to go wrong there, and the chain was hefty enough to have graced a medium-sized motorbike. But as a means of propulsion they had one great advantage over a lightweight modern machine – the farm dogs left you well alone. Ordinarily, their only amusement was to chase passing cyclists down the road, but when I came along they would jump up on the wall as normal, barking furiously, but then go quiet and slink back into the yard at the site of an old black bicycle ridden by someone wearing black Wellington boots. I confess to being rather thankful that the local postman obviously gave them short shrift if they came within reach of his toecap.

During the course of my mapping I traced some spectacular staurolite-kyanite schists into what is now known as the Ox Mountains shear zone. My aim in those days was to estimate peak metamorphic P-T conditions (in the mid-70's this seemed like a novel idea) and so I was keen to find samples with multiple co-existing and unaltered metamorphic minerals. When I got back and studied the thin sections I realised that the rocks that had even the slightest hint of the secondary fabric that distinguishes the shear zone, never had any fresh biotite left. In the most altered rocks there was widespread chlorite and muscovite with barely a trace of original porphyroblasts, but in an intervening zone secondary chloritoid was present in pseudomorphs after garnet, staurolite or kyanite, with paragonite and margarite in addition to muscovite and chlorite. Outside the shear zone, high grade assemblages were preserved because no water had got at them when they were experiencing greenschist facies conditions, while in the main part of the shear zone sufficient water had penetrated to convert the rock into one that was stable in the presence of water at greenschist facies temperatures. Between, where reaction was incomplete, the low variance assemblage reflected restricted water influx and may have buffered water pressure below lithostatic.

I was first alerted to the wider geophysical significance of petrological observations of retrogression by *Fred Vine* while we were colleagues at the University of East Anglia. *Fred* was working on the electrical conductivity of the crust, and at that time, in the mid 1970's, a number of groups had reported unexpectedly high electrical conductivity from stable, old lower continental crust. The obvious explanation was that the lower crust was wet, but if so, would that water not react with its hosts? It only took some back of the envelope calculations to show that the chemical potential of water in equilibrium with coexisting remnant high grade anhydrous phases and their hydrated products under normal crustal conditions would be so small that it could not possibly correspond to the presence of free fluid – the fluid pressure would just be a bar or two, and so the pores containing it would rapidly collapse. Since the electrical conductivity measurements, if due to water, would require several percent of interconnected water, there had to be another cause for the conductivity anomaly. Subsequently I revisited the problem with *John Valley* during a study leave in Madison, Wisconsin (Yardley and Valley, 1997) and looked at a wider range of rock types and fluid compositions. The answer was always the same; C-O-H-salt fluids of any description cannot coexist with amphibolite or granulite facies assemblages under greenschist facies conditions. This presupposes that equilibrium is attained, but hydration reactions appear to be very fast at these conditions. More recently I have been able to investigate this myself, thanks to an invitation from *Wilhelm Heinrich* to work in his group at GFZ Potsdam, and confirmed that it is the case (Yardley *et al.,* 2010, 2014).

4.4 High-T Geothermal Fields

Geothermal systems are not only an important class of crustal fluids in their own right, they also provide remarkable insights into metamorphic and ore forming processes since they can be accessed and sampled while high temperature fluid-rock interactions are in progress. The development of continental geothermal fields producing energy from flashing of superheated water drove the development of major new areas of geochemistry starting in the 1960's, but it was many years before geochemists and geologists working with ancient rocks woke up to the opportunities and insights that the new work on geothermal geochemistry was opening up. It is now apparent that much of the development of minerals such as chlorite, epidote and carbonates in ancient igneous rock is not just an irritating distraction to frustrate igneous petrologists, but provides a record of large scale water circulation through the crust, especially in the vicinity of active volcanoes and other areas of high heat flow. Work in Iceland, New Zealand and the USA in particular revolutionised our understanding of hydrothermal alteration in geothermal fields (Browne, 1978; Arnórsson *et al.*, 2007) and many of the key players moved seamlessly between work on geothermal systems and studies of epithermal ore deposits, which were recognised as originating in geothermal environments. The publication of the volume edited by Henley *et al.* (1984) in an Economic Geology publication series encapsulated this philosophy.

As noted above, it is rare to be able to sample fluids that are responsible for metamorphism. An important exception to this is in the Salton Sea geothermal field in southern California. Here, deep geothermal wells extend to >7,000 feet (>2,100 m) and reach temperatures of 360 °C that are well within the greenschist facies of metamorphism (Muffler and White, 1969). Minerals characteristic of the greenschist facies, including chlorite, epidote, K-feldspar, albite, K-mica and quartz are produced by interaction of the fluids with sands, silts and clays that originally filled the basin. Thermodynamic modelling shows that the geothermal fluids in this system can originate from just the chemical interaction of Colorado River water with sediments as temperature and pressure increased (Helgeson, 1968). Importantly, water-rock interactions in the Salton Sea geothermal field are producing CO_2 as one of the products, and CO_2 is also common in many medium to high-grade metamorphic environments. Moreover, the geothermal fluids achieve very high total dissolved salt contents, up to 45,000 ppm (45 wt.%), and the source of the salinity is thought to be the dissolution of evaporite deposits in the subsurface.

With the recognition of mid-ocean ridge (MOR) hot springs (Corliss *et al.*, 1979) we suddenly had natural analogues that explained a range of phenomena that had puzzled geologists for many decades, such as the spilite problem – where did albite basalts come from and why were they always altered? The amount of hot water that circulates through MOR hydrothermal systems today is about 3×10^{13} kg/a (Elderfield and Schultz, 1996) out of a total mass of the oceans of around 1.4×10^{21} kg. Since this seawater carries a significant dissolved load of chloride salts and other components, MOR systems will always be the dominant sites of metasomatism in the crust. MOR systems draw in ocean water of constant composition, and discharge a modified fluid which is diluted and dispersed in the ocean. MOR hydrothermal systems are examples of single pass geothermal systems in which the crust is progressively modified as it equilibrates with seawater. In contrast, much geothermal circulation in the continental crust takes place in multi-pass systems in which water recirculates through pyroclastic horizons in the upper crust, hydrating the volcanogenic material and progressively reacting with it. It is probably unhelpful to talk of high temperature geothermal systems approaching equilibrium, because fluid circulation requires a temperature gradient, as well as the addition of magmatic volatiles into circulating groundwater. This precludes the possibility of full attainment of chemical equilibrium. This is evident in the systematic evolution in alteration mineralogy as hydrothermal systems associated with igneous intrusions evolve (Lowell and Guilbert, 1970; Beane and Titley, 1981). But local equilibration between hydrothermal minerals and fluid is probably quite widespread. Boiling provides a further challenge to the achievement and long-term maintenance of equilibrium because gas species may partition into the vapour phase very rapidly compared to the rate at which mineral – fluid interactions can compensate for the resulting changes in fluid chemistry.

4.4.1 Continental geothermal systems and epithermal mineral deposits

As noted earlier, we have a reasonably good understanding of the compositions of fluids in continental geothermal systems because these fluids are directly accessible and can be sampled. And just as we have learned much about the fluids associated with formation of Mississippi Valley-type (MVT) ore deposits through studies of basinal (oil-field) brines, so too have we learned about ore-forming processes in epithermal environments from studies of active continental geothermal systems. The time when I (RJB) was student in the late 1970s and early 1980s was also the time that the genetic link between geothermal activity and epithermal precious metal deposits was being cemented. Publications with titles such as “Guide to the Active Epithermal (Geothermal) Systems and Precious Metal Deposits of New Zealand” by Henley *et al.* (1986), and “The geothermal framework for epithermal deposits” (Henley, 1985), “Ore metals in active geothermal systems” (Weissberg *et al.*, 1979), “Epithermal Gold/Silver Deposits: The Geothermal Connection” (Bonham and Giles, 1983) all helped to clarify and further define the genetic link between continental geothermal activity and epithermal precious metal mineralisation.

Fluid inclusions contributed significantly to the geothermal/epithermal connection for two main reasons. First, in active geothermal systems fluid inclusions provided a record of the past history of the system, and thus changes in the physical characteristics (temperature, presence or absence of boiling, etc.) could be documented. In the fossil systems (epithermal deposits) fluid inclusions provided the only record of the fluid history associated with the formation of the deposits. Fluid inclusion studies of active systems can help in reservoir assessment by identifying areas of cold-water inflow, different fluid sources, and whether the system is still heating or has entered a cooling cycle. These studies have further confirmed the presence of low salinity, Na-K rich fluids of dominantly meteoric origin in most continental geothermal systems. However, even within a single volcanic hosted geothermal system, fluids with widely varying physical and chemical properties can be found, including highly acidic sulphate-rich and/or carbonate-rich fluids, neutral pH chloride fluids ± boiling, and cooler dilute chloride fluids (Henley and Hedenquist, 1986). Moreover, many studies documented the temporal evolution of the systems. For example, Sasada *et al.* (1986) documented that in the Hohi geothermal system, Japan, early fluids were high temperature and were boiling, and as the system evolved boiling ceased and the fluids cooled. In some locations, extensive boiling was assumed owing to the presence of relatively high salinity fluid inclusions. Simmons and Browne (1997) also found evidence for extensive boiling producing high salinity brines in the Broadlands-Ohaaki geothermal system, New Zealand.

A critical observation from both active continental geothermal systems and their fossil equivalents, the epithermal deposits, is that fluid boiling occurred at some time during the evolution of the system. Recognition of boiling was important for three reasons. First, from a fluid inclusion perspective it meant that the measured homogenisation temperature of the inclusions was equal to the trapping temperature, *i.e.* no pressure correction was needed (see Roedder and Bodnar, 1980). Secondly, the presence of boiling meant that the fluid inclusions were trapped on the liquid-vapour (or vapour pressure) curve. Thus, assuming that the composition of the inclusion could be determined and that appropriate PTX phase equilibria were available, the formation pressure of the fluid inclusion could be estimated. This, in turn, could be used to infer a formation depth (see more about this below).

Perhaps the most significant implication of the presence of boiling in the geothermal-epithermal environment was that it provided a mechanism to deposit gold and silver to form the high-grade bonanza ores that often characterise these deposits. In many such deposits, the bottom of the ore zone is sharp, with gold and/or silver grades sometimes dropping from several troy ounces of gold per tonne, or several thousands of grams of silver per tonne, to grades that are near the limits of detection. Clearly, changes in fluid properties such as temperature or pH or oxygen fugacity that occur more gradually in time and space would not produce the sharp discontinuity in grade that is observed. However, if an upwelling fluid transporting gold or silver suddenly begins to boil, the solubility of precious metals could decrease instantly by several orders of magnitude. For example, consider a non-boiling fluid at 250 °C that is in equilibrium with quartz, adularia and illite at a pH of ~6.3 and oxygen activity of about 10^{-35}. The solubility of gold in this solution would be ~500 ppb. If the fluid boils and begins to deposit amorphous silica (as evidenced by the ubiquitous occurrence of colloform banded quartz associated with epithermal gold and silver mineralisation), the pH will drop to ~5.1 and gold solubility will decrease to ~10 ppb. Thus, if the fluid before boiling is transporting >10 ppb Au, gold will be deposited as soon as boiling begins. This process is repeated multiple times at slightly different depths along the vein as the system continuously seals by quartz deposition and boiling ceases, followed by later fracturing and re-opening of the vein to initiate a new phase of boiling and gold deposition. The total tonnage is a function of the number of boiling events, and exploration geologists look for evidence of multiple episodes of brecciation or fracturing when exploring for epithermal precious metal deposits. Experimental studies (Stefánsson and Seward, 2003, 2004) are consistent with this relationship between boiling and precious metal deposition.

Perhaps one of the most definitive tests of the relationship between boiling and precious metal deposition in the epithermal environment comes from a field experiment conducted by *Kevin Brown* of the University of Auckland (Brown, 1986). Deep (non-boiling) geothermal fluids in the Broadlands-Ohaaki geothermal field contain ~1.5 ppb Au and 8 ppb Ag, with both gold and silver transported as sulphide complexes. To test the efficiency of boiling as a depositional mechanism for gold and silver in this environment, Kevin replaced one of the back-pressure plates in a geothermal well with a new plate. As hot, non-boiling geothermal fluid rises through the well delivering the fluids to the power plant it passes through a small orifice in the back-pressure plate where pressure drops from several tens of bars to ~ 1 bar and the fluid boils or "flashes" to steam. After 44 days, *Kevin* removed the back pressure plate from the well, and observed a brass-colored precipitate on the upflow (low pressure) side of the plate. *Kevin* analysed the precipitate and found that it was mostly chalcopyrite but also contained 4-6 mass % Au and 2.5-30 mass % Ag. Thus, a small bonanza Au-Ag deposit was formed at the boiling interface, from fluids that had very low Au and Ag concentrations in the deep, non-boiling part of the system.

As noted above, when fluid inclusions are formed in a boiling system, the homogenisation temperature corresponds to the trapping temperature and this information can be used along with known PTX phase equilibria for the fluid to estimate the trapping pressure. In epithermal deposits, fluid inclusion homogenisation temperatures are generally ≤300 °C and may be as low as about 150 °C. Assuming that the fluid is pure H_2O, the pressure on the liquid vapour curve at these temperatures ranges from about 86 bars (300 °C) to ~5 bars (150 °C). When converted to depths assuming a cold water hydrostatic pressure gradient, these pressures correspond to depths ranging from ~850 m to 50 m at the time of mineralisation. In some cases, these depths are reasonable based on the known geology (and topography) at the time of mineralisation. However, in other cases the shallow depths were difficult to reconcile with the geological history of the area. The solution to this dilemma came when it was recognised that fluid inclusions from epithermal deposits often contain small amounts of carbon dioxide that are not easily detected during petrographic examination or microthermometry (Bodnar *et al.*, 1985b; Hedenquist and Henley, 1985). For an H_2O-CO_2 inclusion to contain both liquid and vapour CO_2 at room temperature it must contain at least 2.43 mole % CO_2. Similarly, for the fluid inclusion to form CO_2 clathrate ($CO_2 \cdot 5\,¾\,H_2O$) during cooling, it must contain an amount of CO_2 equivalent to a CO_2 partial pressure of ~5-10 bars (several tenths of a mole percent). However, with these small amounts of CO_2 it is unlikely that the clathrate phase would be recognised during the cooling of the inclusion. The presence of relatively small amounts of CO_2 could, however, be recognised during crushing studies (see Fig. 5.13 in Bodnar *et al.*, 1985b) and today could be detected by Raman analysis. An examination of fluids and fluid inclusions from active geothermal systems and from their fossil equivalents, the epithermal deposits, show CO_2 contents ranging from a few tenths to a few mole percent (Bodnar *et al.*, 1985b, 2014).

The recognition that fluid inclusions in epithermal deposits often contain small amounts of CO_2 (Hedenquist and Henley, 1985; Bodnar *et al.*, 1985b), combined with available PTX phase equilibria for the system H_2O-CO_2-NaCl, made it possible to determine the pressures (and depths) of formation of fluid inclusions in epithermal deposits, and these revised depths were more consistent with geological reconstructions. For example, a CO_2-free, 5 wt.% H_2O-NaCl fluid would boil at a depth of ~450 m at 250 °C. Addition of 0.5 mole% CO_2 to the fluid lowers the depth of boiling to nearly 1,200 m, or nearly three times as deep and more consistent with inferred erosional histories in many deposits. The development of more sensitive analytical tools, combined with the availability of experimentally-determined data for the PVTX properties of H_2O-CO_2-NaCl made it possible to refine the interpretation of fluid inclusions and to better reconcile the fluid inclusion data with the geology.

4.5 Magmatic Fluids

Rising magma bodies are the main pathways for bringing fluids from the mantle and deep crust to the Earth's surface. A range of fluid components, including carbon dioxide and salts, as well as water itself are somewhat soluble in silicate melts and increase in concentration as the magma crystallises, exsolving once saturation is reached. The importance of volatile species in magmas has been recognised by both magmatic and ore deposit geochemists for many years and there have been a number of important contributions in recent years. This is a field which we have watched with interest, and to which RJB has contributed to in various ways. Below we summarise the current state of knowledge based on our personal experiences plus many excellent published results.

From the perspective of crustal fluids, magmatic fluids provide short-lived, but sometimes intense, events which may be quite distinctive. Magmas are relatively dense compared to C-O-H fluids, and magmas crystallise within the crust at pressures that are effectively lithostatic. Fluids exsolving from the crystallising magma are also at lithostatic pressure, and are trapped beneath the crystallising rock rind above the magma – Burnham (1979, 1997) refers to this zone as the water-saturated carapace. Owing to the very large difference between the partial molar volume of water in the melt (~18 cm^3/mole) and the molar volume of the water after it exsolves from the melt (~50-90 cm^3/mole), pressure within the water-saturated carapace quickly exceeds the tensile strength of the overlying rock, causing it to fracture with the release of fluids into the overlying rocks (Bodnar *et al.,* 2007). This process happens repeatedly as the magma cools and crystallises, giving rise to the characteristic breccias and vein systems that occur in the upper portions of the pluton and overlying coeval volcanic rocks in arc-type systems associated porphyry-type ore deposits. Initially, magmatic fluids are unable to mix with local groundwaters because of the large pressure difference, but once the pressure has been released, magmatic components may be incorporated into circulating ground waters. While the amounts of magmatic water in the hydrothermal circulation cell are likely to be small relative to the amounts of external (meteoric) water, other volatile components such as S, Sb and As are so rare in meteoric groundwater that they provide efficient markers of the magmatic volatile contribution.

Magmatic fluids, like other deep waters, may contain significant quantities of dissolved salts and their behaviour has been the subject of extensive research. As well as contributing to metal transport and ore formation, chloride salts also extend the range of P-T conditions over which liquid and vapour phases can coexist, allowing phase separation to take place at pressures approaching 2 kbar (Sourirajan and Kennedy, 1962; Bodnar *et al.*, 1985a; Pitzer and Pabalan, 1986). The basic patterns of behaviour of chloride fluids in a magmatic environment were worked out first in an ore deposit context (Holland, 1972; Burnham, 1979; 1997; Candela and Holland, 1984; Cline and Bodnar, 1991), and there is now a wealth of data on the compositions of fluid that can evolve from intermediate to acid melts as they crystallise. Latterly, igneous geochemists have begun to appreciate that magmatic fluids are better treated as chloride-rich brines.

While most emphasis has been on chloride-bearing magmatic fluids and these play a central role in the generation of many types of ore bodies, it is also worth noting out that not all magmatic fluids are dominated by H_2O and salts. Cameron *et al.* (1953) pointed out that some granite pegmatite fluid inclusions contain low salinity H_2O-CO_2 fluids. These may contain high concentrations of other soluble gases. As we noted earlier, the fact that both brines and low-salinity, gas-rich fluids can be present in a range of geological settings is a reflection of the fluid phase equilibria (Fig. 1.1) rather than a special geological characteristic of the source region.

The dissolved load of magmatic fluids is influenced by the source region, by the lithologies encountered during ascent, and by the conditions under which crystallisation takes place. In general, the salinity of exsolved fluids depends on both the amount of salt and water present in the melt, and the depth at which crystallisation occurs (Cline and Bodnar, 1991). It may also be influenced by the rocks encountered during ascent; for example Campbell *et al.* (1995) reported that very saline fluids (effectively wet salt melts) released by the Capitan Pluton, New Mexico, contained salt remobilised from evaporites through which the magma had ascended.

4.5.1 Magmatic-hydrothermal mineral deposits

Arc volcanism occurring at active continental margins associated with subduction processes represents one of the two most significant (along with mid-ocean ridge systems) environments for cycling of mass and energy from the Earth's interior to the surface. Intermediate composition magmas produced in this setting, and the related hydrothermal systems, are associated with many important ore deposit types, including 1) porphyry Cu-Au-Mo deposits, 2) base and precious metal skarn deposits, and 3) base and precious metal epithermal deposits. These magmatic systems also provide the thermal energy that drives the continental geothermal systems that produce most of the geothermal electricity on Earth. These various ore deposit types and active geothermal systems have been the focus of many studies, and much of our understanding of the physical and chemical properties of fluids in these systems comes from studies of fluid inclusions.

Porphyry copper (Au-Mo) deposits are associated with intermediate composition (granodiorite) magmas emplaced into the crust above subducting slabs. It is now reasonably well known that the metals in the deposits are sourced from the magma and are transported from the melt into the magmatic fluid phase as the magma cools, crystallises and rises to shallow levels in the crust (Bodnar, 1995b; Audétat *et al.*, 2008). The efficiency of metal extraction from the melt phase is related to many factors, including but not limited to the salinity (chloride content) of the exsolving magmatic fluid. The salinity, in turn, is related to the initial chloride content of the melt as well as the pressure of exsolution. In most porphyry copper deposits a high salinity aqueous fluid is associated with mineralisation. One of the earliest reports of the relationship between highly saline fluids and copper mineralisation was by Lindgren (1905) who noted *"They [halite-bearing inclusions] prove, I think conclusively, that the acid porphyry magma [at Morenci] was accompanied by notable quantities of aqueous solutions containing a large quantity of salt which probably was NaCl."* and that *"It is perhaps a significant fact that these inclusions are absent in the diorite porphyries, which as a rule have no connection to the copper deposits."* The many fluid inclusion studies of porphyry copper deposits that have been conducted in the 100+ years since Lindgren's observation have indeed confirmed that highly saline fluids and copper mineralisation are related.

Early studies of porphyry copper deposits confirmed the presence of abundant Na and K in the ore-forming fluids, based on optical identification of halite (NaCl) and sylvite (KCl) daughter minerals in the inclusions (Roedder, 1971a). More recently, the introduction of analytical techniques such as laser ablation ICP-MS has confirmed that Na and K are among the most abundant cations in the fluids, but have also shown that Fe is sometimes the second-most abundant cation and that porphyry-forming fluids should more appropriately considered to be (Na,K,Fe)Cl brines (Bodnar *et al.*, 2014). Laser ablation ICP-MS has also allowed us to quantify the minor and trace element abundances in the fluids, especially the important ore metals. These studies suggest that copper contents can reach concentrations of several tens of thousands of ppm (a few weight percent), demonstrating the efficiency of the fluids to scavenge and transport metals from the magmas to the developing ore deposit.

RJB writes – The first in depth study of fluid inclusions in porphyry systems was by *Ed Roedder* (Roedder, 1971a), who studied inclusions from the Bingham, Utah, and Butte, Montana porphyry Cu-Mo systems, and the Climax, Colorado porphyry moly system. In the paper that resulted from this work, *Roedder* was remarkably prescient in making observations and interpretations that laid the groundwork for future studies and contributed to the development of a genetic model for these deposits. *Roedder* recognised the presence of halite and sylvite as daughter minerals in fluid inclusions and constructed a ternary H_2O-NaCl-KCl diagram to interpret the inclusions and determine the Na/K ratio of the fluids. This diagram, with modifications based on more recent experimental data, is still used today to interpret inclusions from porphyry (and other) systems. *Ed* also used data from the fluid inclusions to estimate mineralisation pressures, which could then be used to infer formation depths. This application very much intrigued me (RJB) a few years later when, as a student, I was working on a porphyry system and was trying to determine the pressures and depths of mineralisation. My many questions to *Ed* about how to use inclusion data to determine pressures led to our collaboration to write what has become a highly-cited paper on geologic pressure determinations (Roedder and Bodnar, 1980). The final observation that *Ed* reported that was unexpected was the occurrence of trails of vapour-rich fluid inclusions, without coexisting halite-bearing inclusions. It had been previously recognised that fluid phase immiscibility is a common occurrence in porphyry systems, producing coexisting high-salinity brine and low-salinity vapour. Based on the absence of halite-bearing fluid inclusions with some assemblages, *Roedder* surmised that the vapour-rich inclusions might represent a high-temperature, low salinity fluid that exsolved from the magma and did not undergo immiscibility. Today, it is generally accepted that early in the evolution of porphyry magmas the PVTX conditions are such that the exsolving aqueous fluid is in the one-phase vapour (or gas) field (Henley and McNabb, 1978; Bodnar, 1995b; Lecumberri Sanchez *et al.*, 2013; Bodnar *et al.*, 2014), and fluid inclusions that trap this early fluid would be vapour-rich when observed at room temperature. These, and other observations made by *Roedder*, significantly advanced our understanding of fluid evolution associated with not only porphyry copper deposits, but with epizonal intermediate composition plutons in general.

In my (RJB) own study of the porphyry copper deposit at Red Mountain, Arizona, I applied many of the same techniques used by *Roedder*, and I attempted to make many of the same interpretations and estimates of pressures and depths as *Roedder* had done. At the time, there was little data available in the literature to construct the PVTX diagrams needed to interpret the fluid inclusion microthermometric data, and much of what was available was questionable or internally inconsistent. This led to my interest in conducting experiments to determine the PVTX properties of saline aqueous fluids at high temperature and pressure, and eventually led me to Penn State where *Wayne Burnham* was the acknowledged North American expert in conducting fluid PVTX experiments at elevated PT conditions. At the time, the only other researcher routinely doing such work was *E.U. Franck* in Karlsruhe, Germany, and I had the opportunity to meet *Professor Franck* when he came to Penn State to visit *Wayne Burnham* while I was a student. At this time, *Franck's* student *Richard Hilbert* was completing an experimental study of the PVTX properties of H_2O-NaCl for salinities up to 25 wt.%, and so I decided to focus on the more NaCl-rich part of the system and determined the PVTX properties of 30, 50, and 70 wt.% NaCl fluids to 900 °C and 5 kbar. With *Hilbert's* data and my data for higher salinities, we now had the basic experimental data needed for a rigorous interpretation of the microthermometric data being obtained from high salinity and high temperature fluids in porphyry-type ore deposits.

5.

WHAT NEXT?

In the course of this *Perspectives* we tried to outline a wide range of science with which we have been involved, and provide some insight into some related areas that are outside our personal experience. Now that we have advanced our understanding of crustal fluids to the point that we understand the composition of some important types of crustal fluids, and have some knowledge of the composition of a much wider range of fluids, what's next? We see several areas where we may expect significant advances in the not too distant future.

- During our careers we have witnessed remarkable advances in analytical techniques that allow us to analyse increasingly smaller samples and with ever-increasing precision and accuracy. When we were starting as students, the state-of-the-art for stable isotope analysis of minerals was by bulk analysis using conventional ratio mass spectrometry. This evolved to analysis of spots as small as a few tens of microns by SIMS. Today we can analyse spots as small as a micron by nanoSIMS. Similarly, when we were students, fluid inclusion analyses were conducted by crushing large bulk mineral samples, extracting the fluid from hundreds of thousands of inclusions and assuming this represented the composition of the "fluid" from which the mineral precipitated. During our careers, these bulk techniques were first miniaturised to cope with smaller samples containing single inclusion populations, then microanalytical techniques such as PIXE, PIGE, synchrotron-based XRF and laser ablation ICPMS were introduced and perfected to allow measurement of major and trace elements in individual fluid inclusions on the order of ten microns in size. This ever-increasing reduction in required sample volume has identified unrecognised heterogeneities in isotopic and elemental composition that has in turn led to an improved understanding of the complexity of natural systems. In the future we expect sample size requirements to be reduced further, while at the same time analytical precision and detection limits will improve, allowing a wider range of trace elements to be analysed and perhaps allowing meaningful stable isotope measurements on individual fluid inclusions. In the more distant future, radiogenic isotope analyses of individual fluid inclusions may permit geochronology studies on individual fluid events, such as ore-formation, which would have an unprecedented impact on our ability to constrain durations of geologic processes.
- The amazing advances in our ability to analyse geologic samples that we have experienced during our careers, has been paralleled by significant advances in our ability to simulate natural processes using numerical models. While the theory to conduct such simulations has advanced somewhat during the past few decades, the major factor that allows us to simulate complex natural processes is enormous improvement in computing power. This has allowed us to couple the physical and chemical processes

that we have described in detail in this *Perspectives* to more completely understand the interplay between the physical and chemical environments. Thus, coupled fluid flow and water-rock interactions are providing an improved understanding of processes associated with submarine hydrothermal systems, as well as fluid-mediated processes in continental crust environments, such as those associated with geological storage of carbon dioxide.

- Throughout this *Perspectives* we focused on the properties of bulk fluids and mostly invoked experimental and theoretical data that are based on physical and thermodynamic properties of bulk fluids. However, it is becoming increasingly apparent that properties of fluids in thin films can differ drastically from those of the bulk fluid – thus surface chemistry is and will continue to play an increasingly important role in studies of natural systems, especially in the deeper parts of the crust where any free fluids that are present will likely occur as films that are only several molecular layers in thickness. We expect the thermodynamic database and numerical models to simulate fluid-rock interactions in the crust to incorporate these important effects in the future.
- Another area which we believe is ripe for advance is in the application of our knowledge of fluids into other areas of Earth Science, both pure and applied. Whether it be the rheology of the crust or the partitioning of elements into magmas, our results for fluid compositions and behaviour have major implications for cognate fields and it is essential that we help develop an interdisciplinary understanding of crustal fluids. Taking this a step further, much of the information and techniques developed by Earth Scientists has application to wide range of problems in materials science, chemical, civil and environmental engineering, and even the life sciences. Thus, it is critical in today's interdisciplinary and multi-disciplinary research environment that we reach out to workers in these other fields to share our expertise as well as to learn from them. We have already noted here that research in geological carbon storage draws on the same understanding of fluid behaviour that we use in purely academic studies. The same techniques and approaches are also applicable more widely, wherever the geosphere is involved in large scale engineering projects, for example the search for geological disposal facilities for radioactive waste has been particularly important in the development of geochemical modelling.

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ROBERT J. BODNAR is the C. C. Garvin Professor and a University Distinguished Professor at Virginia Tech. His research is related to the occurrence, properties and role of fluids in the Earth and planetary environments, and involves experimental, theoretical and laboratory studies. He is an ISI "Highly Cited Researcher", has received the Lindgren Award and Silver Medal from the Society of Economic Geologists, N.L. Bowen Award from the American Geophysical Union, and is a Fellow of the American Geophysical Union, American Association for the Advancement of Science, Society of Economic Geologists, Mineralogical Society of America and Geological Society of America. In 2009, Bodnar was awarded an honourary degree (*Laurea Honoris Causa*) from the University of Napoli Federico II, in Naples, Italy. When not doing science, Bob enjoys playing racquetball, running, listening to classic rock & roll, driving sports cars too fast, and playing with his menagerie of dogs and cats.