WHO CARES ABOUT EQUILIBRIUM?

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ABSTRACT

Drilling has yielded much information about the subsurface geology of geothermal systems. It has also opened insights into the evolution of large tectonically and volcanically active regions, for example the Taupo Volcanic Zone (Milicich et al, 2013; Wilson et al, 2010). However, active geothermal systems are also large natural laboratories. Some of their characteristics are revealed through fieldwork, examining cores and cuttings, output and production data, measuring down hole temperatures and pressures, analyzing thermal fluids and reservoir modeling. Our knowledge of processes that affect the physical, chemical and mineralogical properties of rocks and thermal fluids has increased several fold since Fenner's (1936) brave but dangerous exploratory drilling in Yellowstone National Park in the 1930's. His pioneering research was greatly extended after the War when successful exploratory, production and research drilling was begun at the Wairakei field (Thain and Carey, 2009) and later at other geothermal prospects in New Zealand, Iceland, USA, Mexico, Japan, Indonesia, the Philippines and Kenya.

1. NATURAL AND THE EXPERIMENTAL LABORATORIES

The geological community, notably the geochemists and mineralogists, has been a major beneficiary of geothermal exploration. Because many of the rocks that host geothermal reservoirs are of volcanic origin they readily react with thermal fluids. These reactions affect both the minerals originally present in the rocks and the compositions of the fluids themselves. However, in many instances the reactions on both micro- and macro- scales are incomplete so equilibrium between minerals and between minerals and fluids is seldom achieved. Instead, petrologists see the products as incomplete, or 'frozen', reactions. Non-equilibrium is an anathema to experimental chemists and metamorphic petrologists but it is a fact of life for geothermal petrologists. However, except when applying chemical geothermometry, whether equilibrium is achieved or not is almost inconsequential. Geothermal petrology has progressed largely by ignoring it, preferring instead to apply an empirical or pragmatic methodology. This has given insights into understanding the hydrology of geothermal systems and also yielded information about processes that affect fluid/rock relations.

Geothermal systems can deliver information about factors that control the stability (or meta-stability) of many minerals. Few minerals that occur in active geothermal systems are rare and even wairakite, first recognized by Alfred Steiner (1955) of the NZ Geological Survey, is quite common. Many minerals occur also in other geological environments, such as in low to mid- grade metamorphic rocks and hydrothermal ore deposits. This has allowed geothermal lessons to be applied more widely. However, geothermal systems are open and long lived, allowing large volumes of fluid, with their dissolved constituents to through flow whereas experiments conducted in laboratories are usually (but not always) closed systems designed so equilibrium can be achieved. A limitation of these experiments is that their time spans are necessarily short. Even some of the famous experiments (e.g. Hemley, 1959) that revealed the relationships between minerals in the important K_2O-Na_2O-Al_2O_3-SiO_2-H_2O and the CaO-K_2O-Al_2O_3-SiO_2-H_2O systems were mostly made at temperatures above 300^0C and the equilibrium boundaries between the minerals involved have had to be projected to match the temperatures prevailing in geothermal systems. On the other hand, geothermal systems are large scale, whereas experiments conducted to determine the stabilities of minerals commonly use only milligrams of reactants. In practice, our understanding of the genesis and stability of hydrothermal minerals and, more generally, the significance of fluid/mineral interactions, has been built upon both observations made of geothermal systems and the results of well planned laboratory experiments (e.g. Seward, 1973; Mountain and Sonney, 2010).

NON-EQUILIBRIUM IN THE NATURAL LABORATORY

There are several examples of non-equilibrium in active geothermal systems. However, here I consider only hydrothermal alteration and mineral deposition that occurs in response to processes that affect a thermal fluid. Although three types of hydrothermal alteration occur in geothermal systems these result from only two quite different processes.

Replacement alteration. This occurs when a hydrothermal mineral replaces a primary or earlier formed hydrothermal mineral. The new mineral is a product of interactions between the earlier mineral and the fluid. The precursor mineral is unstable in the new environment and responds to it by trying to transform to a stable phase through exchanging constituents with some of those present in the surrounding fluid. The identity of the secondary mineral so formed depends on several factors conditional on the geothermal system itself and the relative stabilities of the primary minerals-evidence for the different fluid/mineral reaction rates. Some minerals are temperature sensitive; for example, wairakite is stable above 210^0, epidote above 250^0 and actinolite above about 290^0. Other replacement minerals provide, subjectively anyway, guidance about permeability; replacement adularia occurs where permeability is highest but the presence of albite indicates lower permeability. It seems also that the type of host rocks in the reservoir does not play a major role in controlling the identities of the hydrothermal minerals that form, although there are some exceptions to this generalization.

Sometimes it is uncertain if the secondary mineral truly replaces its precursor or merely occupies the space from which it was dissolved. On other occasions, however, there is little doubt that replacement has indeed taken place; for example, albite that partly replaces andesine preserves its parent's twins. Chlorite that has replaced pyroxene may inherit the original twinning and optical zoning. Some replacement reactions involve two ions, for example, for albite to replace andesine requires not only Na^+ ions to replace Ca^{2+} ions but an accompanying replacement of Al^{3+} by Si^{4+}.

Leaching. This is also a type of hydrothermal alteration that results from fluid/mineral interactions. Leaching is not common in the explored parts of geothermal systems, which are usually within the fluid upflow or outflow domains, but it occurs in places, particularly where acid steam condensate or magmatically derived water reacts with minerals present in the host rocks. Cavities created by dissolution of plagioclase can be recognized from the ghost forms of dissolved euhedral crystals.

Hydrothermal minerals deposited into open space. Vein and vug fill minerals record processes that affect the fluid and have little, if anything, to do with the identities of the host rocks. They are analogous to minerals that form as scales in slotted liner or other pipe work.

Mineralogical evidence for non-equilibrium. An obvious indication of non-equilibrium between thermal fluids and minerals is incomplete replacement reactions between primary and secondary minerals evident in thin section. It is very common to see, for example, andesine partly replaced by adularia, illite, albite, calcite, wairakite or even three or more of these minerals. Similarly, clinopyroxene may be partly replaced by chlorite, epidote, calcite, titanite or/and pyrite plus leucoxene. Clearly the secondary minerals are not in equilibrium with the reacting fluid(s); nor are the minerals likely to be in equilibrium with one another. An extreme example of non-equilibrium is replacement of albite or adularia by kaolin. It is impossible, under geothermal conditions, for these minerals to co-exist in equilibrium since their stability fields are separated by that of K-mica. If you wish to become frustrated try to write balanced equations for some of these reactions. In any case, replacement reactions are of equal volume rather than of conserving mass; also if you are a traditionalist, forget about the phase rule. Other evidence for non-equilibrium is the optical and chemical zoning of minerals such as epidote, sphalerite, secondary plagioclase and, more commonly, banding in veins and vugs. However, the direction of a reaction is evident in thin section and, in practical terms, this is the information that is used to help interpret hydrology.

Boiling and mineral deposition. An example of a non-equilibrium condition is boiling. Boiling is a traumatic event for ascending water and causes it to change composition. The event is reflected in the mineralogy of veins that form at the sites of boiling. The geochemists took the lead in understanding the boiling process many years ago by showing, for example that a 2% loss of the mass of a volume of boiled water resulted in an 70 % loss of the amount of CO_2 previously dissolved in it, together with a large proportion of dissolved H_2S (Ellis, 1962). They also showed (Mahon et al, 1980) that even a small amount of CO_2 gas dissolved in the liquid greatly lowered its boiling temperature. Boiling causes the residual liquid to degas, become both more saline and slightly more alkaline as well as to cool. These consequences may cause 3 minerals to form as veins at the sites of boiling:

(a) Calcite deposits because of CO_2 loss. For reasons not entirely certain this has a bladed morphology (but see Tulloch, 1982; Simmons and Christenson, 1994).

(b) Quartz deposits because the fluid cools.

(c) A potassic phase deposits because of the slight increase in pH. Boiling moves the aK^+/aH^+ ratio of a typical, partly degassed thermal water towards, or over, the illite/K-feldspar stability boundary into the adularia field.

Thus the usual mineralogical consequence of boiling is deposition in veins of quartz, bladed calcite and adularia although each of these three minerals deposits for entirely different reasons.

The sites of boiling within a reservoir migrate in both time and space since boiling causes cooling and the loss of CO_2 means that the residual liquid is no longer on its appropriate boiling point for depth curve. As the then partly degassed, but now slightly more saline, liquid continues to ascend it reaches a shallower depth where it encounters T-P-CO_2 conditions that cause it to boil again and so the process is repeated. Subsequently, in an open system (which geothermal systems are), an ascending thermal fluid boils episodically at different depths appropriate to its salinity, gas content and pressure at a particular time. Fluid flow paths change as channels become restricted through mineral deposition but others open as a result of micro-fracturing, hydraulic fracturing or possibly induced by thermal stress or seismic events.

The time component. Time is a parameter that cannot be easily simulated in a laboratory. It presents a different problem for those who view geothermal systems as natural laboratories. This is because little is known about the time spans of geothermal systems. However, they have a birth and a death and we seek to exploit them somewhere in between these two events. In reality, we are looking only at a small episode during a lifetime, on a scale of rather like passing someone in the street. Petrography shows that during their lifetimes, conditions change constantly within a reservoir, as evidenced by mineral overprints, mineral zoning, cross-cutting veins and vein para-genesis. There are, in effect, multiple and changing conditions of non-equilibrium. There are also hints, and even some evidence, that geothermal systems may last for several thousand to hundred of thousands of years. Larderello and Steamboat Springs have had some level of thermal activity for the past 3 million years or so (White, 1979). This does not mean that the intensity of thermal activity has remained unchanged and indeed it is not possible that this could happen. Even during the past hundred years or so activity at some fields has declined markedly without human interference (Hochstein et al, 2008 for Tokaanu). Some progress has extended our knowledge about the duration of thermal activity, however; for example, Moore et al (2000) published an important paper showing multiple episodes of hydrothermal alteration have occurred at the Tiwi field over a period longer than 300,000 years.

WHERE EQUILIBRIUM *IS* IMPORTANT: THE CONTRIBUTIONS OF THE GEOCHEMISTS TO GEOTHERMAL PETROLOGY

A major advance in geothermal science and our knowledge of thermal fluids has been made by the geochemists, especially those based at Chemistry and Nuclear Science Divisions, DSIR, at both Wairakei (Tony Mahon, Richard

Glover, Kevin Brown, Richard Henley, Bruce Christenson) and Petone (Jim Ellis, Rainer Gougel, Terry Seward, Byron Weissberg, Werner Giggenbach) and also another outstanding group at the USGS in Menlo Park (Robert Fournier, Alfred Truesdell, Donald White, Patrick Muffler). Their work had great practical benefit that influenced the course of geothermal exploration and production but also had parallel benefits to understanding hydrothermal ore deposits. It greatly advanced geothermal petrology by providing excellent analytical data and by treating minerals as thermodynamic entities. It is true that the geochemists were more concerned with equilibrium than the petrologists but their time scales differed and pragmatism rightly dominated. This was evident in the development of the chemical geothermometers that proved so effective in exploration and production. The geochemists at Chemistry Division, DSIR and those at the USGS, Menlo Park, initially developed the silica and alkali geothermometers quite independently (rather like Darwin and Wallace recognizing evolution by natural selection and Leibnitz and Newton simultaneously inventing calculus). Although there are now several chemical and isotope geothermometers the early ones have lasted the distance. The silica geothermometer requires that thermal waters at depth be in equilibrium with a silica phase, usually quartz and the alkali geothermometers assumes equilibrium between the fluid and albite and K-feldspar. I think the mere presence of these minerals is sufficient as reactions between them and the waters are probably fast. There are several other assumptions, of course, and there are now several more sophisticated chemical geothermometers, thanks to the penetrating insights of Werner Giggenbach (e.g. 1988) but equilibrium on the geochemical scale is a condition of their use too.

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