APPLICATION OF MINERALOGICAL METHODS TO ASSESS THE THERMAL STABILITIES OF GEOTHERMAL RESERVOIRS

Patrick R.L. Browne
Geothermal Institute and Geology Department
University of Auckland, Private Bag 92019
Auckland, New Zealand

ABSTRACT
Estimates of temperatures, past and present, in geothermal reservoirs can be made by using now standard mineralogical techniques, including fluid inclusion geothermometry, vitrinite reflectance, calc-silicate and clay occurrence, the extent of clay interlayering, and measuring clay crystallinity. Recent studies of clays in 60 drillcores from 6 wells at Wairakei, for example, show an inverse relationship between reservoir temperatures and crystallinities from 90° to 225°C (195 to 435°F) (Kübler Indices: 1.40 to 0.44 A-28). Fluid inclusion geothermometry results require careful interpretation but the method need not be calibrated with respect to the reservoir, as do other geothermometric methods.

More useful are mineral geothermometers and methods that are of wider application, and some of these are summarized in this paper. For convenience, the thermal signatures of a geothermal reservoir may be considered, in mineralogical terms, as belonging to one of three categories:

1. minerals whose presence in a reservoir has a thermal significance;
2. minerals whose compositions or structures vary with temperature;
3. determinative methods that depend upon some property of a mineral or material present within the reservoir rocks.

TEMPERATURE SENSITIVE MINERALS

INTRODUCTION
Measuring temperatures directly in geothermal wells is obviously an essential part of reservoir assessment. However, in several situations, downwell temperatures are not necessarily the same as those that prevailed immediately prior to drilling as this disturbs the thermal regime and often promotes changes in the patterns of fluid flow. Many wells never reach thermal equilibrium with their reservoir even months after being drilled. Discharge of a well also irrevocably changes temperatures at depths shallower than its feed zones.

For these reasons, indirect estimates of subsurface temperatures made independently can be very useful. In addition, by comparing geothermometric results obtained by using different methods with one another, and with temperatures measured directly, we can assess the thermal stability of a geothermal reservoir, or at least some sections of it.

This paper reviews some of the mineralogical methods available for assessing reservoir temperatures but excludes both fluid and isotope geothermometers.

METHODS
Several methods proposed for estimating temperature have been applied or tested in natural geothermal systems. Some have proved unsuccessful, e.g. Al in hydrothermal quartz (Scotford, 1975; Browne and Wodzicki, 1977), or apply only under very restricted circumstances, e.g. sphalerite and pyrrhotite geothermometers (Kissin and Scott, 1982; Scott and Barnes, 1971).

Among calc-silicates that are not zeolites, the presence of epidote has long been used to indicate temperatures in excess of 240°, and in some reservoirs its crystal size and abundance increases with increasing temperature (Elders et al., 1981; Browne and Gardner, 1982). Prehnite is usually stable above 220°, hydrothermal amphibole above 290°, and calcium garnet above about 320°.

A few non calc-silicates show a thermal sensitivity that may also be useful in interpreting reservoir temperatures: hydrothermal biotite usually occurs above about 320°, for example, and cristobalite below 150°.
A different assemblage of hydrothermal minerals forms in the presence of acidic fluids; at 250°C, these typically produce pyrophyllite, diasporo, and alunite (Reyes, 1990). It is important to realize that the identities of the hydrothermal minerals which form are largely independent of rock type, and that reservoir temperatures can only be interpreted from the presence of a mineral in a core or cutting. The converse, i.e. the absence of a hydrothermal mineral, cannot be cited as evidence that a specific temperature was not reached. This is because the stability of many hydrothermal minerals depends not only upon temperature but also on other factors. For example, the formation of many calc-silicates is prohibited where the altering fluids contain high concentrations of dissolved carbon dioxide.

The other group of minerals whose presence has often been used to interpret temperatures is the clays, all phyllosilicates, with essential (OH)'.

Near neutral pH alkali chloride waters react with the host rocks, or deposit directly from solution, to form a thermally progressive sequence of minerals. Typically, montmorillonite occurs to about 140°C, mixed layer clays from 140 to about 210°C, with illite or sericite stable at higher temperatures (Browne, 1979). This sequence differs slightly from place to place; for example, montmorillonite prevails to 230°C in Icelandic (Kristmannsdóttir, 1975) and to 180°C in Philippine geothermal systems (Reyes, 1990).

Where the altering fluids are acidic the sequence, with respect to temperature, is: kaolinite occurs to 120°C; dickite ± kaolinite from 120 to 200°C; dickite and pyrophyllite from 200 to 250°C; and pyrophyllite ± illite from 250 to 320°C (Reyes, 1990).

In many geothermal reservoirs, chlorite occurs over a wide range of temperatures and its presence generally offers no useful geothermometer, but in the basaltic rocks of Iceland it occurs only above 230°C (Kristmannsdóttir and Tómasson, 1976).

MINERALS WHO COMPOSITIONS OR STRUCTURE VARY WITH TEMPERATURE

Interlayered clays

Alteration zones characterized by mixed layer clays occur in many geothermal systems and the extent of interlayering can usually be related to reservoir temperature. Mixed layer clays are present in several Iceland geothermal fields, for example, where the measured temperatures are between 200 and 230°C (Kristmannsdóttir, 1975). In New Zealand geothermal fields the proportion of illite interlayered with montmorillonite usually increases with temperature above about 100°C until only illite is present above about 200°C.

Recent work (Harvey and Browne, 1991) shows that there are slight but measurable differences in the extent of interlayering within samples from the same depth. These differences can be related to clay size in that fractions less than 0.2μm may contain a higher proportion of the smectite interlayer component than co-existing clays larger than 0.2μm in diameter (Figure 1).

Figure 1: Sequence of mixed-layer clays present in cores from drillhole WK207 compared with the measured downwell temperatures that most closely match the estimated predrilling temperatures (from Harvey and Browne, 1991).

Measuring the extent of interlayering and, indeed, identifying the clay minerals present requires use of an X-ray Diffractometer. Other instruments useful in characterizing clay minerals include Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), and Infrared Spectroscopy. For example, DTA patterns of samples recovered from drillholes at the Ngawha geothermal field, New Zealand, show progressive changes with increasing temperature (Browne and Gardner, 1982; 1985). The reactions the endothermic peaks in these patterns represent can be clearly attributed to the hydration states of the clay minerals they contain. Samples from depths where the measured temperatures are less than 120°C to 180°C have a larger endothermic peak at about 150°C and a smaller one at about 550°C. Samples from hotter locations give DTA patterns with progressively smaller low temperature peaks but proportionally larger ones at 580°C (Fig. 2). Samples from depths where the reservoir temperatures are above 180°C, however, are almost thermally inert even though some contain appreciable amounts of illite and chlorite. By contrast, chlorite from Icelandic geothermal systems commonly give DTA patterns with large endothermic peaks at 620°C (Kristmannsdóttir, 1975).

Solid solution series

The extent of solid solution among non-stoichiometric hydrothermal minerals has long been recognized as being controlled, at least partly, by temperature. At temperatures prevailing in geothermal reservoirs, for example, the orthoclase content of coexisting albite and adularia provides a usable geothermometer above about 250°C (McDowell and McCurry, 1978; Hedenquist and Browne, 1989) but one which has not yet been fully tested.

Potentially more useful, because chlorite is much more widespread than coexisting feldspars, is the chlorite geothermometer (Cathelineau and Nieva, 1985; Cathelineau, 1988) which relies on the temperature dependence of the amount of tetrahedral aluminum incorporated within chlorite. This geothermometer was applied successfully at the Los Azufres and Salton Sea...
Table 1: Summary features of mineralogical geothermometers commonly applied to geothermal reservoirs

<table>
<thead>
<tr>
<th>Minerals or Technique</th>
<th>Method</th>
<th>Effective Temperature Range (°C)</th>
<th>Provisos</th>
<th>Records</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occurrence of calc-silicates</td>
<td>Thin section examination</td>
<td>best 200 to 320</td>
<td>Inappropriate where altering fluids have high concentrations of dissolved CO₂</td>
<td>Usually peak temperatures; textural relations show thermal changes</td>
</tr>
<tr>
<td>Occurrence of clay minerals</td>
<td>XRD</td>
<td>-100 to 220</td>
<td>Different clay types depending on fluid pH</td>
<td>Usually peak temperatures attained for considerable period</td>
</tr>
<tr>
<td>Extent of clay interlayering</td>
<td>XRD</td>
<td>-140 to 220</td>
<td>Slight differences depending on clay size. Not applicable to acid alteration</td>
<td>Usually peak temperatures attained for considerable period</td>
</tr>
<tr>
<td>Crystallinity of montmorillonite, illite and their interlayers</td>
<td>XRD</td>
<td>130 to 230</td>
<td>Not applicable to chlorite or kaolins</td>
<td>Peak temperature attained for considerable period</td>
</tr>
<tr>
<td>Composition of chlorite</td>
<td>electron microprobe</td>
<td>? &gt;200</td>
<td>Promising method not yet fully established</td>
<td>Temperature at the site of analysis</td>
</tr>
<tr>
<td>Feldspar compositions</td>
<td>electron microprobe</td>
<td>&gt;250</td>
<td>Co-existing feldspars needed</td>
<td>Temperature at the site of analysis</td>
</tr>
<tr>
<td>Fluid inclusion geothermometry</td>
<td>heating stage, microscope</td>
<td>&gt;100</td>
<td>Powerful method but needs careful interpretation of data</td>
<td>Temperatures at site of inclusions. With sufficient data, changes in the thermal regime can be recognised</td>
</tr>
<tr>
<td>Vitrinite reflectivity</td>
<td>reflected light microscope</td>
<td>&gt;100</td>
<td>Requires rocks containing carbonaceous material. Field specific</td>
<td>Peak temperature attained for minimum period of 10-100 years</td>
</tr>
</tbody>
</table>

XRD = X-ray Diffraction  
DTA = Differential Thermal Analysis  
IRS = Infrared Spectroscopy

Figure 2: Differential Thermal Analysis charts of selected core and cutting samples from Ngawha drillhole Ng 18, showing typical variations in thermal reactions of samples from depths where measured temperatures differ (from Browne and Gardner, 1985).
Clay crystallinity

A technique commonly used by petrologists working on low grade metamorphic rocks is to measure the crystallinity of any clay minerals present. This is a straightforward method but has seldom been applied to geothermal materials, except in a qualitative way. The crystallinity measurements are made by determining the width, at half peak height, of the (001) reflections of illite and illite/smectite and the (002) reflection of chlorite. Units used are degrees 2θ and the crystallinity is commonly termed the Kubler Index.

Recently, Chi Ma et al. (1992) reported the Kubler Indices for clay minerals present in 60 cores of lacustrine sediments from 6 drillholes in the Te Mihi sector of the Wairakei Geothermal Field. The crystallinity of the illite/smectite mixed layer clays increases with increasing temperature and depth (Fig. 3). Most Kubler Indices range from 1.40 to 0.44 Δ 2θ, where measured reservoir temperatures are between 90° and 225°C (irrespective of host rock), giving the relationship

\[ T(°C) = 249 - 89.3 \times K.I. \]

where K.I. is the Kubler Index (Fig. 4).

By contrast, the crystallinity of chlorites present in the same samples do not vary with reservoir temperature (Fig. 4).

Chi Ma et al. (1992) found no measurable difference between the crystallinities of the larger (0.2 to 2.0 μm) and smaller (<0.2 μm) size clay fractions.

Comparison of temperatures measured in drillholes and from fluid inclusions allows even slight changes in reservoir temperatures to be recognized. For example, the northern sector of Waiotapu and the eastern sector of Broadlands-Ohaaki have cooled by 20°C or more since quartz crystals there grew (Hedenquist and Browne, 1989; Hedenquist, 1990). The Ngawha geothermal reservoir shows evidence, from fluid inclusion studies, for cooling of its southern margin but heating by 20°C or so of its northern margin since the time the inclusions formed (Browne and Gardner, 1982).

Fluid inclusion geothermometry can thus reveal the direction of thermal evolution of a geothermal reservoir. However, because the ages of the inclusions are rarely known, the rate at which temperature changes occur can not be determined.

Usually, liquid only is trapped in inclusions, and the homogenisation temperatures measured on inclusions that trap two phases are much higher than the actual trapping temperatures and thus erroneous. Another problem is caused by "necking of inclusions" after they form, whereby an inclusion separates into two or more inclusions, usually with different proportions of vapor and liquid that then give spurious homogenisation temperatures. Straightforward statistical analysis of data will lead to incorrect conclusions. Hence, an operator needs to show sound judgement in interpreting fluid inclusion data.
However, fluid inclusion geothermometry is easier to apply to geothermal systems than to other geological environments. Pressure corrections are seldom needed, for example, or can be determined directly from drillhole measurements. The distinctions between primary, secondary and pseudosecondary inclusions are of lesser consequences than elsewhere. Indeed, Youngman (1985) has shown that usable secondary (i.e. geothermal) inclusions occur in primary minerals in the Wairakei system.

The homogenisation temperatures of vapor-rich inclusions are seldom able to be measured because of the difficulty of seeing when homogenisation occurs. However, the mere presence of vapor-rich inclusions demonstrates that the crystals grew under vapor phase conditions, and this information is often important in assessing reservoir temperatures and pressures. It also demonstrates that boiling occurred during their formation.

Vitrinite Reflectivity

This is a powerful method for estimating temperatures in geothermal reservoirs that contain sediments or tuffaceous sediments with carbonaceous material. Although vitrinite reflectivity is a standard technique used for many years by sedimentologists, especially those working on oil reservoirs or coal deposits, the method has only recently been applied to geothermal reservoirs. Barker and Elders (1981) pioneered the application of this method by studying fluvial sediments comprising the Cerro Prieto reservoir. They showed that vitrinite reflectivity of samples from several wells increases regularly with depth and temperature. Once a relationship between reflectivity and temperature was established, i.e. a vitrinite geothermometer calibrated, this knowledge was then applied to estimating reservoir temperatures using samples as they were recovered from later drillholes. The vitrinite reflectivity method has also been applied successfully to lacustrine sediments at the Wairakei and Ngatamariki geothermal systems (Struckmeyer and Browne, 1988; Gonzales, 1985) in New Zealand and Palinpinon in the Philippines (Hermoso, 1991).

Note that a reflectivity versus temperature calibration curve is system-specific and these curves are not transferable from field to field since reflectivity values depend also on the duration of heating (but see Barker, 1991).

COMPARISON OF MINERALOGICAL THERMOMETERS AND TECHNIQUES

Table 1 summarises some of the salient features of the mineralogical geothermometers and techniques commonly used to evaluate geothermal reservoirs. All methods offer opportunities that are independent of one another, and all have limitations. Obviously, the most important of the latter is first having suitable material. Some methods, such as those relying on chlorite and feldspar compositions, show much promise but are not yet fully established. Both require analyses to be made on an expensive electron microscope.

All the methods described here, except measuring the homogenisation temperatures of fluid inclusions, essentially rely on calibrations made, either in natural systems or in a laboratory. Uncertainties in the natural systems often arise in deciding how close the measured drillhole temperatures are to the predrilling or true reservoir temperatures. This results from the nature of drilling itself, which introduces cool drilling fluids into a hotter reservoir and disturbs irrevocably its fluid flow patterns. Many geologists do not always carefully evaluate the quality of drillhole measurements nor the circumstances under which the data were obtained. This means that some of the temperature stability ranges assigned to thermally sensitive minerals are likely to be in error. Errors are likely to be greatest at shallowest depths where reservoir temperatures are usually coolest and temperature gradients steepest. In fact, any temperatures measured at shallow depths in wells that have discharged should not be used to calibrate mineral geothermometers. Even temperature control experiments should be used with caution as equilibrium is achieved only very slowly at low temperatures.

Calc-silicates are usually detected easily by petrographic microscope, and their distribution should be recorded as part of any routine assessment of a reservoir. Some minerals, e.g. epidote, are reliable temperature indicators, irrespective of rock type or field, but others, such as prehnite, have lower temperature stabilities that vary from field to field but remain uniform within each field. The petrographic microscope is also the most important instrument to recognise thermal changes that have occurred within a reservoir. This is done by observing alteration overprints or the sequences of hydrothermal minerals that occur in veins or vugs, and interpreting them with respect to the temperatures they indicate.

Fluid inclusion geothermometry does not rely on field calibration, and also offers a fairly precise tool for determining changes in temperature within a reservoir. This can be done by careful observations of the growth directions within individual fluid inclusions, with all calibrations based on a single inclusion, the temperature stability of which is system-specific and these curves are not transferable from field to field but remain uniform within each field. The petrographic microscope is also the most important instrument to recognise thermal changes that have occurred within a reservoir. This is done by observing alteration overprints or the sequences of hydrothermal minerals that occur in veins or vugs, and interpreting them with respect to the temperatures they indicate.

In reality, a single homogenisation temperature tells us only the temperature (albeit precisely) within an area the size of the individual inclusion (~10 μm) at an unknown time. By contrast, the vitrinite geothermometer commonly recalls (much less precisely) the peak temperatures a sizable section of a reservoir has attained for periods as brief as 10 to 100 years (Barker, 1991). This is because cooling has no effect on vitrinite reflectivity.

Clay minerals also seldom record retrograde thermal effects except where they overprint hydrothermal feldspars, and these may be due to either cooling, a lowering of fluid pH, or both. Clay crystallinity, the proportions of montmorillonite and illite interlayered together in a single phase and the occurrence of the clays probably also reflect the maximum temperatures attained but, again, for an unknown but "considerable" period. This is because of the slow thermal response of reservoir rocks, since catalysing or reacting fluids do not usually move freely in rocks containing abundant clays.

Chlorite crystallinity has no thermal significance at Wairakei, in contrast to the crystallinity of co-existing interlayered illite/montmorillonite, but whether or not this conclusion applies elsewhere is not known.
In summary, however, the combination of mineralogical techniques and present knowledge of mineral occurrences offers important ways for determining the thermal stability of a geothermal reservoir.

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REFERENCES


