

NOTES

RELATIONSHIP BETWEEN ILLITE CRYSTALLINITY AND TEMPERATURE IN ACTIVE GEOTHERMAL SYSTEMS OF NEW ZEALAND

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INTRODUCTION

Illite crystallinity (IC), widely used to evaluate variations in metamorphic conditions, primarily depends on temperature (*e.g.*, Kisch, 1983; Frey, 1987). IC is determined by measuring the half-peak-width of the 10-Å illite peak on oriented mineral aggregate preparations of the <2- μm size fractions (Kubler, 1967, 1968), and is expressed in $^{\circ}\Delta 2\theta$. Over the past three decades, major advances were made in the study and understanding of illite crystallinity. The effects of sample preparation (Krumm and Buggisch, 1991), instrumental conditions and interlaboratory standardization and calibration (Kisch, 1990, 1991), and measured precision and reproducibility (Robinson *et al.*, 1990; Warr and Rice, 1994), represent some of these advances in technique. Although methods more advanced than the IC method for sample characterization have been developed recently, such as the integral peak width method (Drits *et al.*, 1997) and the Warren-Averbach method (*e.g.*, Eberl *et al.*, 1998), the IC method still remains a most suitable monitor of very low-grade metamorphism of clastic sedimentary rocks. However, the factors that precisely control crystallinity are not known. Active geothermal systems are especially fruitful places to study the genesis of clay minerals since these environments are natural laboratories where fluid/rock interactions occur under measurable conditions.

Illite is abundant and occurs at temperatures >160°C in active geothermal fields of New Zealand. Host rocks are mainly andesitic to rhyolitic lavas and pyroclastics. In this study, we correlate crystallinity values of illites in cores recovered from two wells, drilled into two active geothermal systems, with the measured drillhole temperatures. Hence, we can evaluate factors that may influence the crystallinity of illites.

The Taupo Volcanic Zone is one of the most active volcanic regions on earth; the area has experienced volcanic and tectonic activity for at least one million years (Wilson, 1993). Because of this activity, geothermal systems occur throughout the area and were extensively studied. Ohaaki-Broadlands and Waiotapu are two of the best studied in the zone (Figure 1); they are located within a sequence of near-horizontal Quaternary to Recent rhyolitic lavas and pyroclastic rocks, overlying a Mesozoic greywacke and argillite basement. Hydrothermal fluids ascend along steeply dipping normal faults, interconnected joints, and hydraulic fractures. We studied core samples from drillhole number BR12 at the Ohaaki-Broadlands system and WT7 at Waiotapu. Both drillholes encountered rocks with well-developed sequences of illitic clay minerals, and were cored at intervals of ~30–50 m.

WELL DATA

Drillhole BR12 has very low permeability and was unable to sustain a continuous discharge, although it did discharge for 14 d (New Zealand Ministry of Works and Development, 1977). The best permeability, as revealed by well tests and circulation losses that occurred during drilling, was at a depth of 1090 m where the fluids evidently move in channels within a welded ignimbrite. Tuffs, mainly rhyolite lapilli tuffs, were the other rocks encountered within the studied zone (700–1373 m). Measured downwell temperatures are below boiling and lie between 160°C (at 700 m) and 285°C (at 1373 m) and pressures are near hot hydrostatic.

The hydrothermal minerals accompanying illite include albite, calcite, pyrite, quartz, chlorite, and trace amounts of pyrrhotite and adularia. These phases are in equilibrium or nearly so, but they are not in equi-

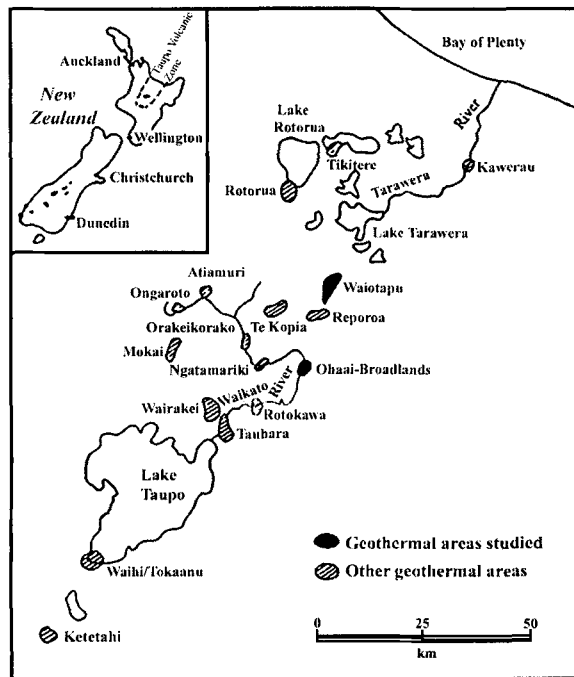


Figure 1. Map showing the locations of geothermal systems studied in Taupo Volcanic Zone, New Zealand. Modified from Henly *et al.* (1986).

librium with primary andesine which survives in places. The secondary feldspars and illite are also in equilibrium with the thermal fluid, which is discharged by the well (Browne and Ellis, 1970). The Na/K molecular ratio of the this fluid is about 13.0 and the deep fluid plots within the K-mica stability field. However, the ratio plots close to the albite-adularia boundary at 260°C in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system (Browne and Ellis, 1970).

Drillhole WT7 has a fairly uniform permeability throughout, but it has a slightly higher permeability below 915 m (Dench, 1963). During an output test,

the well discharged 85 tons per hour of water and steam at 5.5 bars gauge pressure at 880 Joules/kg, an output equivalent to 2.5 MW. Pressures measured downwell were between 70–92 bars (at well bottom). Most common rock types encountered were rhyolitic tuffs and breccias, welded in places, and also andesite at depths from 816 to 930 m. Other hydrothermal minerals include varying proportions of quartz, calcite, chlorite, adularia, albite plus minor leucocene, titanite, and pyrite with trace amounts of pyrrhotite (Hedenquist and Browne, 1989). Some of the illite occurs as a late replacement of secondary adularia (Hedenquist and Browne, 1989). The discharged waters have Na/K molecular ratios between 13.4–15.0 and the compositions also lie within the stability field of illite (Hedenquist and Browne, 1989).

The main differences between conditions in WT7 and BR12 are the temperatures (Table 1). The hydrothermal minerals and lithologies are the same in both the intervals studied, except for the presence of andesite at Waiotapu. However, Browne (1989) showed that hydrothermal-alteration mineralogy of the active geothermal systems of New Zealand is nearly independent of the host rock. The slight differences in the Na/K ratios of the reservoir fluids are not judged to be significant, as these differences are controlled by the presence of secondary feldspars in the reservoir rocks. However, the compositions of both fluids are within the stability field of illite (Browne and Ellis, 1970; Hedenquist and Browne, 1989). The fluids from BR12 have higher bicarbonate contents (1196 mg/kg) than those from WT7 (147 mg/kg) but the two wells have chloride contents that are nearly the same (1196 mg/kg for BR12 and 1260 mg/kg for WT7) (New Zealand Ministry of Works and Development, 1977; Wilson, 1963).

The duration of geothermal activity at both Ohaaki-Broadlands and Waiotapu is unknown, but the intensity of the pervasive hydrothermal alteration at both

Table 1. Crystallinity values of illite and chlorite of cores from drillholes BR12 and WT7.

| Well | Depth (m) | Lithology | Temperature (°C) | Clay minerals | $\text{IC}_{\text{AD}}^{\text{illite}}$ (°Δ2θ) | $\text{IC}_{\text{GL}}^{\text{illite}}$ (°Δ2θ) | $\text{ChC}_{\text{AD}}^{\text{chlorite}}$ (°Δ2θ) | $\text{ChC}_{\text{GL}}^{\text{chlorite}}$ (°Δ2θ) |
|------|-----------|------------|------------------|-------------------|--|--|---|---|
| WT7 | 345 | Ignimbrite | 230 | Illite | 1.04 | 0.73 | — | — |
| WT7 | 451 | Ignimbrite | 240 | Illite + chlorite | 0.77 | 0.60 | 0.24 | 0.20 |
| WT7 | 560 | Ignimbrite | 255 | Illite + chlorite | 0.71 | 0.57 | 0.23 | 0.22 |
| WT7 | 777 | Ignimbrite | 278 | Illite + chlorite | 0.60 | 0.55 | 0.32 | 0.32 |
| WT7 | 879 | Andesite | 290 | Illite + chlorite | 0.56 | 0.47 | 0.29 | 0.29 |
| WT7 | 940 | Ignimbrite | 292 | Illite + chlorite | 0.47 | 0.34 | 0.27 | 0.24 |
| WT7 | 1005 | Ignimbrite | 295 | Illite + chlorite | 0.47 | 0.39 | 0.27 | 0.22 |
| BR12 | 700 | tuff | 160 | Illite | 1.33 | 0.78 | — | — |
| BR12 | 793 | tuff | 190 | Illite | 1.04 | 0.73 | — | — |
| BR12 | 931 | tuff | 220 | Illite | 0.60 | 0.47 | — | — |
| BR12 | 1188 | tuff | 264 | Illite + chlorite | 0.65 | 0.55 | 0.21 | 0.19 |
| BR12 | 1235 | tuff | 270 | Illite + chlorite | 0.55 | 0.47 | 0.24 | 0.22 |
| BR12 | 1373 | tuff | 285 | Illite + chlorite | 0.42 | 0.34 | 0.22 | 0.19 |

AD, air-dried samples; GL, glycolated samples; ChC, chlorite crystallinity.

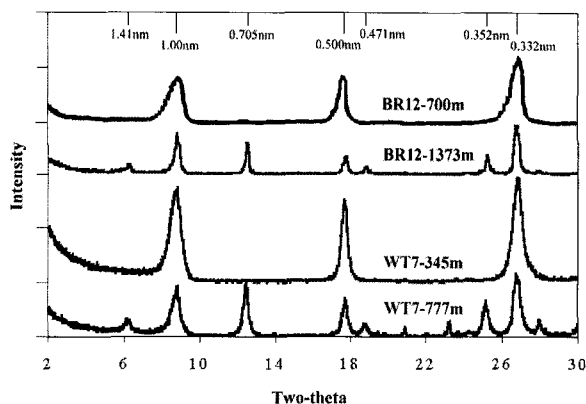


Figure 2. Typical XRD patterns (oriented preparations) of the <2- μm fraction of samples from drillholes BR12 and WT7.

locations suggests that they are long lived and possibly older than 150,000 y (Weissberg *et al.*, 1979). There is evidence that the Kawerau geothermal field, 40 km northeast of Waiotapu (Figure 1), has been active for more than 200,000 \pm 30,000 y (Browne, 1979) and the reservoir rocks have the same intensity of alteration as those at Waiotapu and Ohaaki-Broadlands. The host ignimbrites are 360,000 years old, and thus this is the maximum age of thermal activity at both fields.

METHODS

Separated air-dried clay fractions of all cores from BR12 had been previously X-rayed from 2 to 34 $^{\circ}$ 2 θ using CuK α radiation (Browne and Ellis, 1970). Where necessary, clay fractions were treated with ethylene glycol and/or heated to detect swelling clays and to distinguish between chlorite and kaolinite. The same procedure was followed for cores from well WT7 (Hedenquist, 1983). Based on these earlier results, the <2- μm size fractions from drillholes BR12 and WT7 were identified by X-ray diffraction (XRD) techniques and the IC values measured. The experimental procedures followed the recommendations of the IGCP 294 IC working group (Kisch, 1991).

Each sample was washed, broken into small chips (<20 mm) using a jaw crusher and thoroughly mixed. The rock material was then washed to remove the finest suspension, which may contain mechanically ground crystals produced by the initial crushing. Then the washed rock chips were immersed in 1 L of distilled water and placed in an ultrasonic tank at low frequency (35 kHz) for 3 h. Grain-size separation was achieved by centrifuging the suspension of separated clay, using Stoke's Law. An initial centrifugation was used to separate the >2- μm fraction, and a subsequent centrifugation was used to obtain the <2- μm fraction. The latter produced a clear supernatant.

The <2- μm clay fraction was washed twice in 0.1 N SrCl $_2$ solution; the first wash was allowed to stand overnight, and then cleaned of electrolyte by washing four times in distilled water. The pipette-on-glass technique was used for slide preparation. Glass slides were weighed before and after the application of the clay material and the weight of clay determined. Thick clay preparations (>3 mg/cm 2) were prepared according to Warr and Rice (1994).

The XRD patterns were obtained using a Phillips PW 2243/20 diffractometer at 20 mA and 40 kV CuK α radiation. Each slide was scanned from 2 to 14 $^{\circ}$ 2 θ at a scan speed of 0.6 $^{\circ}$ 2 θ /min and a step width of 0.01 $^{\circ}$ 2 θ , for both air-dried and glycolated preparations.

The crystallinity results of this study were calibrated to the standardized scale (the crystallinity index standard, CIS) of Warr and Rice (1994) by measuring the four sets of pelitic rocks and a single muscovite crystal. The IC scale measured at Auckland was lower than the scale of Warr and Rice (1994), and this is attributed to the use of a 2-mm wide receiving slit and amperage of 20 mA compared to 0.5 mm and 30 mA used by Warr and Rice (1994). IC values given here were converted to the CIS scale by using the following regression equation: $IC_{CIS} = 1.619800 \times IC_{Auckland} - 0.049909$, $R^2 = 0.9899$.

RESULTS

The distribution of clay minerals identified in samples from drillholes BR12 and WT7 are given in Table 1, together with data on sample lithology and formation temperature considered to be closest to pre-drilling conditions. Illite and chlorite are abundant in the <2- μm size fraction (Figure 2). Illite is most abundant and occurs at temperatures above \sim 160 $^{\circ}$ C; chlorite is present where drillhole temperatures are >230 $^{\circ}$ C, but chlorite is most abundant at temperatures near 300 $^{\circ}$ C.

The illite-crystallinity values range from 1.33 to 0.42 $^{\circ}$ Δ 2 θ (air-dried samples) and 0.78 to 0.34 $^{\circ}$ Δ 2 θ (glycolated samples). The glycolation of samples causes a decrease in IC owing to the presence of expandable mixed layers. There is a consistent narrowing of the illite peak of glycolated samples relative to untreated samples. The greatest differences between untreated and glycolated samples are in those samples recovered where lower temperatures occur.

The IC values show a systematic correspondence with the measured downhole temperatures; there is a decrease generally with increasing temperature in each geothermal field for both air-dried and glycolated preparations (Figure 3). Curve-fitting analyses suggested that the dependence of the crystallinity of illite on the temperature in these geothermal fields can be expressed as a linear regression (Figure 3).

The crystallinity values of the 7- Å chlorite peak show much less variation in half-peak-width, rang-

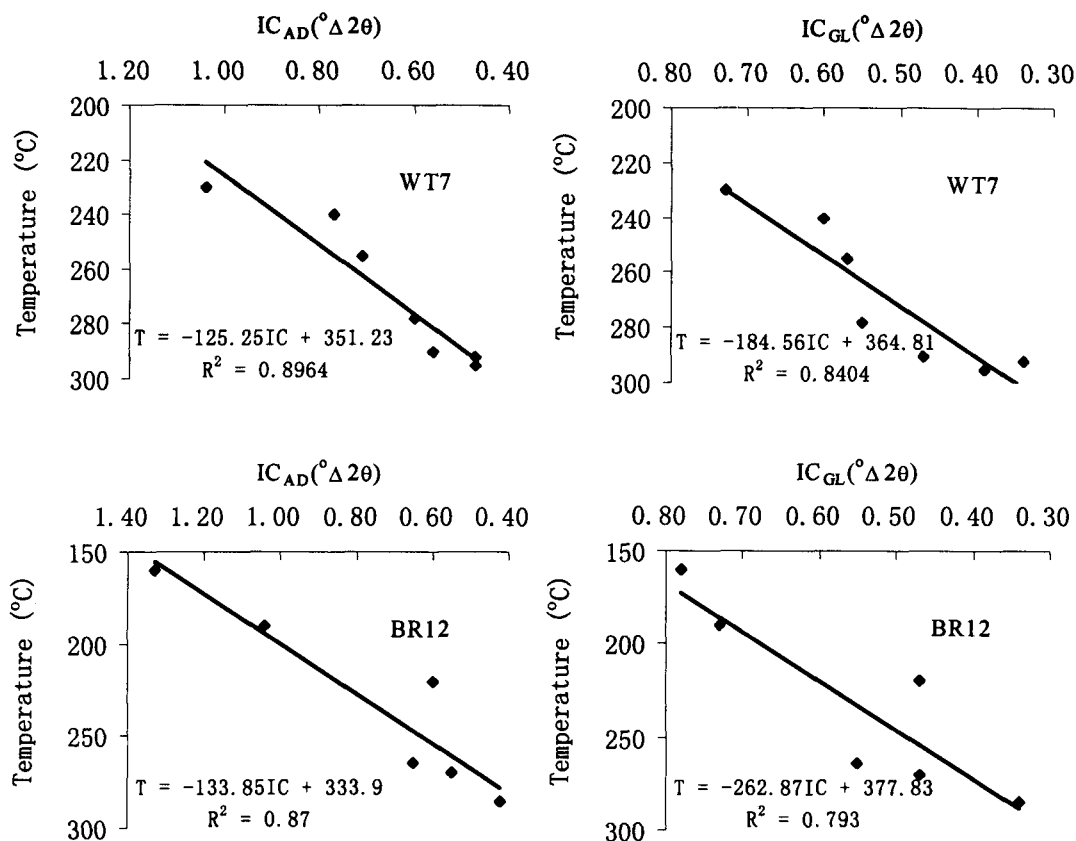


Figure 3. Changes in illite crystallinity values vs. the measured downhole temperatures for cores from drillholes BR12 and WT7.

ing from 0.21 to 0.32 °Δ2θ for air-dried preparations and 0.19 to 0.32 °Δ2θ for glycol-treated preparations, and demonstrate no systematic change with depth (Table 1). The number of expandable layers in chlorites is negligible, as deduced from the small differences between the air-dried and glycolated preparations. Chlorites display narrower peaks than illites in any given sample, indicating that chlorites are generally better crystallized than illites in the same sample.

DISCUSSION

Clay-mineral crystallinity studies published since the pioneering work of Weaver (1960) and Kubler (1967) suggest that temperature is the most important factor influencing crystallinity (e.g., Frey, 1987). The close correlation of IC values of illites with the measured temperatures in each well shows that temperature is the principal factor controlling illite crystallinity. However, the crystallinity values of illites from the same temperature regime of different geothermal fields may differ (Table 1; Figure 2), although physico-chemical conditions, such as lithology, potassium

availability, and permeability, are quite similar in drillholes BR12 and WT7.

Illite crystallinity is a very useful parameter for determining the grade of diagenesis and incipient metamorphism in rocks. The lower-crystallinity boundary of the anchizone is 0.42 °Δ2θ. According to data from Table 1, the illites with IC values <0.42 °Δ2θ formed under reservoir temperatures of 280°C in drillhole BR12 and >290°C in drillhole WT7. The temperature for the onset of anchizone is considerably higher than the value of 200°C used as the boundary between diagenesis and anchizone in pelitic rocks (e.g., Frey *et al.*, 1980) and zeolite-bearing volcanic rocks (Winkler, 1979). However, although in these geothermal fields the host rocks vary from andesites to rhyolites, this temperature generally agrees with the formation temperature of the anchizone reported by Weaver and Broekstra (1984) from a study of shale-slate metamorphism in the Southern Appalachians. The sequence of illitic changes is similar to that observed in the sandstones and shales of the Salton Sea geothermal Field (McDowell and Elders, 1980) and further demonstrate

that the influence of lithology on illite crystallinity is negligible at the onset of the anchizone. The formation temperatures for anchizone may vary with location, even in the same rock type. Thus, the contradictory reported boundary temperatures of the anchizone may possibly be the result of different environmental factors experienced.

In the deepest part of BR12 drillhole, illite formed at a temperature of 280°C and has an IC value of 0.42 °Δ2θ, whereas in the WT7 drillhole, the IC values for illites formed at a temperature of ~290°C are only 0.47 °Δ2θ (Table 1). An alternative explanation for the difference in these IC values is that illites occur at greater depth in the BR12 drillhole than in the WT7 drillhole for the same temperature range. However, there is no evidence that fluid pressure affects illite crystallinity. Possibly, the geothermal systems have different ages and this has an effect, but effects from age differences can not be demonstrated here.

CONCLUSIONS

In general, the observed patterns of crystallinity variations of illites in active geothermal fields confirm that temperature is an important control on illite crystallinity. This study also indicates that the formation temperatures for illites with IC value of 0.42 °Δ2θ may vary with location even in rocks with similar lithologies, potassium availability, and permeability. Thus, there is no certain boundary temperature for the beginning of the anchizone.

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