CHEMISTRY OF EPIDOTES AND CHLORITES IN THE TONGONAN GEOTHERMAL FIELD, LEYTE (PHILIPPINES)

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SUMMARY - Chlorites and epidotes in altered andesites from 4 wells in the Tongonan Geothermal Field were analyzed to identify any correlations of compositional variation with measured well temperature. With increasing well temperature, most of the chlorites show increasing Al^{iv} and Fe^{2+} while the epidotes show decreasing Si^{4+} and Fe^{3+} but increasing tetrahedral Al. This is consistent with observed temperature-dependent compositional changes in other geothermal and metamorphic areas and is therefore taken to indicate that chlorites and epidotes are in equilibrium with the present-day fluids. However, chlorites from two of the wells studied show trends opposite to those prevailing elsewhere suggesting that in these cases the minerals were formed by a hydrothermal fluid which could have been hotter than the presentday fluid.

Deviation from changes in the composition of chlorite and epidote observed in other geothermal (and metamorphic) areas is taken to indicate the existence of relict minerals in the hydrothermal alteration assemblage.

1.0 INTRODUCTION

Secondary minerals are reported to show compositional variations with depths and temperature, both in metamorphic and geothermal areas. Clay minerals are the most common hydrothermal minerals in geothermal areas. Chlorite is the next most common sheet silicate and epidote is the most abundant calc-silicate mineral. Chlorites and epidotes have been reported to show changes in composition with respect to bulk rock composition, temperature, and fluid composition (McDowell and Elders, 1980; Cathelineau and Nieva, 1985; *Cavaretta* et al., 1983; Shikazono, 1984; Liou et al., 1985, Bird et al., 1984; Lonker et al., 1993; Beaufort et al., 1992; Sveinbjornsdottir, 1992).

The Tongonan Geothermal Field (TGF) is one of the geothermal areas in the Philippines which have been developed for electric power generation. The andesitic reservoir rock is hydrothermally altered by the circulating hot fluid and is characterized by abundant clay minerals, chlorites and epidote. The hydrothermal alteration in Tongonan is well-studied (Reyes et al., 1988; Scott, 1988) but information on the chemistry of hydrothermal minerals is minimal. This work discusses the chemistry of epidote and chlorite in altered rocks in Tongonan and shows the variation in the chemistry of these two minerals with temperature.

Chlorite, in Tongonan andesite, typically occurs with calcite and iron oxides as a replacement product after ferromagnesian minerals. It also occasionally replaces plagioclase and also occurs as a vug filling mineral, along with quartz. Chlorite occurs as green xenoblastic blades or spherulites with very low relief. Under crossed polars, chlorite exhibits anomalous interference colours ranging from prussian-blue to brown.

In altered Tongonan andesite, epidote/clinozoisite commonly replaces plagioclase phenocrysts and is also found disseminated in the groundmass and forming veinlets in some samples. Epidote forms anhedral to euhedral *crystals* with *short* to elongated prismatic habit (0.5 mm) and radiating fan-shaped aggregates. The grains are commonly pistachio-green with high relief and exhibit anomalous interference colours from *canary* yellow (epidote) to prussian-blue (clinozoisite).

2.0 ANALYTICAL TECHNIQUES

The chemistry of epidote and chlorite was obtained by wavelength-dispersive x-ray analysis on a CAMECA SX50 electron microprobe operated at 15 keV and 25 nA with a beam diameter between 10 to 15 μ depending on the size of the grains to be analysed. Crystal spectrometers (LIF, PET and RAP) were used in the quantitative analyses of major elements but an attached EDS unit and video display were used to assist in mineral identification. Calibration was monitored using a kaersutite standard. Data reduction for background correction was performed using the CAMECA PAP program reference.

The structural formulae for chlorite were calculated on the basis of $O_{20}(OH)_{16}$ Using a program developed by R.C. Price (1993). All Fe was assigned to Fe^{2+} and all the Si was assigned to the tetrahedral sites. The total tetrahedral atoms per formula was then brought to 8 using Al (Al^{iv}). The remainder of the Al (Al^{vi}) was assigned to the octahedral sites, as were the other divalent ions (Fe^{2+}, Mg^{2+}, Mn^{2+}). All the K, Na, and Ca (provided these do not add up to more than 0.5 wt%) were assigned to the interlayer (high valence) sites. For epidotes, the structural formulae were calculated on the basis of 12.5 O and all iron was taken to be ferric iron. Sufficient Al was added to the Si to obtain a stochiometric proportion of 3 in the tetrahedral sites of the ideal formula. The rest of the Al was allocated to octahedral sites.

3.0 RESULTS

3.1 Mineral Chemistry of Chlorite

The unit structure of chlorite consists of regular alternations of negatively charged tetrahedral-octahedral-tetrahedral layer (ie. talc-like layers with composition $Y_6Z_8O_{20}(OH)_4$) with positively-charged brucite-like interlayer, $(Y_6(OH)_{12})$ (Deer et al., 1992). The octahedral sheets are commonly made up of Mg^{2+} and Fe^{2+} with substantial amount of Mn^{2+} and Na^+ and the tetrahedral cations are primarily Si^{4+} and Al^{3+}. Chlorite has the ideal formula $(R^{2+},R^{3+})_{12}(Si, Al)_8O_{20}(OH)_{16}$ where R^{2+} represents the sum of divalent cations and R^{3+} the sum of trivalent cations.

The chlorites analysed are all homogeneous except for some *grains* in well 505D samples. In these samples, the total alkali content (Na, K, Ca) is greater than 0.5 wt% and consequently that have been excluded from consideration in the interpretation that follows. The chlorite *structure cannot* accommodate large quantities of these ions and their presence indicates interlayering with mica and/or montmorillonite or associated carbonate and silicate (Foster, 1962).

The TGF *chlorites* are characterised by slightly low Al^{iv} relative to the Al^{vi} and by a sum of octahedral cations (I.C.) ranging from 10.78 to 11.99, which is not far from the ideal of 12.00. Plot of the chlorite analyses on a diagram designed by Hey (1954) illustrates that the TGF chlorites belong basically to the pynochlorite species with some data points falling in the ripidolite and diabantite fields.

3.2 Mineral Chemistry of Epidote

Epidote $(Ca_2Fe^{3+}Al_2Si_3O_{12}(OH))$ farms a solid-solution series with clinozoisite $(Ca_2Al_2Si_3O_{12}(OH))$. Minor components include Fe^{2+}, Mg^{2+}, and Mn^{2+} which rarely exceeds 0.15 atoms per formula unit (Deer *et* al., 1992).

The Fe-rich endmember is commonly referred to as the pistacite component (Ps) and is defined as: $Ps = Fe^{3+}/(Fe^{3+} + Al^{+6})$ where Fe^{3+} and Al^{+6} are the corresponding number of Fe^{3+} and octahedral Al ions per formula unit.

All of the epidotes from the TGF *are* Fe-rich with Fe^{3+} ranging fkom 0.49 *to* 0.94 cation per formula unit. Most of these epidotes contain minor quantities of Mn (>0.05 atom per unit formula). Pistacite contents range from .19 to .36.

4.0 DISCUSSION

4.1 Compositional Variations in Chlorites

In most cases, there is a scatter in the data within individual samples. This scattering could be attributed to several factors including overestimation of SiO_2 due to inadvertently measuring a mixture of 2 or more minerals and the presence of trace amounts of alkali elements.

A plot of the FeO (wt%) of bulk rock *vs.* chlorite shows that, although scattering of data points occurs, the FeO in the chlorite increases with increasing FeO contents in the bulk rock indicating that the bulk rock composition contributed, albeit in a minor way, to the variation in the chlorite composition.

The most commonly observed variation in the chlorite composition is an increase in Al^{iv} content with increasing temperature (Cathelineau and Nieva, 1985; McDowell and Elders, 1980). Consequently one should expect a complementary result to the decrease in Al^{vi}.

Figure 1A shows plots of Al^{iv} *vs.* measured well temperature. For well 408, a positive correlation is observed between Al^{iv} and measured well temperature applies and this is also for the first two samples from well 505D [505D/C1 (528 m) and 505D/890 (883 m)]. However, for the other samples from well 505D and all the samples from 5R7D a negative correlation is observed. This suggests that the chlorites that were analyzed in these samples were probably formed by a fluid other than that which is circulating at the present time. At a given depth, the earlier fluid had higher temperatures than those associated with the present-day fluid. This is *further* supported by a *report* of a temperature reversal in well 5R7D (Ogena, 1989) at depths of about 1300 m. The chlorite compositions in this well suggest that deepest sample (5R7D/Core 5,2587.0 m) is associated with the lowest temperature and the shallowest sample (5R7D-3815, 1067.3 m) with the highest temperature. This trend is opposite to that observed m well 408 as well as in other geothermal area (McDowell and Elders, 1980; Cathelineau and Nivea, 1985). However, if the chlorite in this well was formed by another fluid whose temperature was steadily increasing with depth, then obviously the deepest sample should plot at a higher temperature than the shallowest sample.

Another *common* variation with depth (and therefore, temperam) *observed* in chlorites from other geothermal areas involves the abundance of Fe^{2+} and Mg^{2+} in the octahedral layer. These increase with temperature (Cavaretta et al., 1982; Lonker et al., 1993; McDowell and Elder, 1980;) and the TGF chlorites show this pattern with increasing temperature. Furthermore, the trend also supports the conclusion that in Wells 505D and 5R7D (except for the chlorites in the shallow portions of 505D), the chlorites were formed by an earlier hotter fluid. Moreover, the Mg^{2+} in chlorites of these two wells is the opposite to that observed in other areas. "Low" temperature chlorites have higher Mg^{2+} contents than "high" temperature chlorites (Figures 1B and 1C). This can be attributed to a higher proportion of Mg^{2+} to Fe^{2+} in the solution at lower temperature because Fe^{2+} is oxidized to Fe^{3+} as the fluid cools, either by boiling or dilution

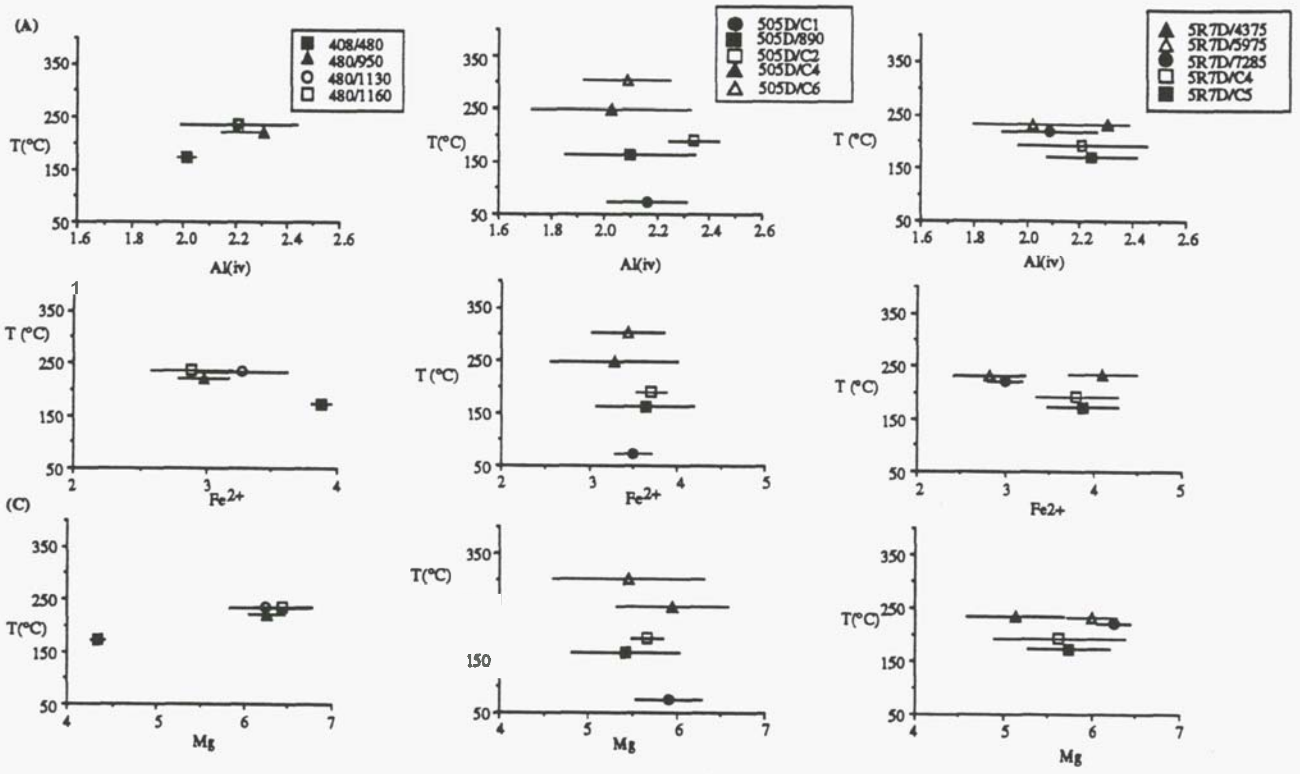

FIGURE 1 Compositional variations in chlorites with measured well temperature. A. Ai (iv) vs. T. B. Fe^{2+} vs. T C. Mg vs. T.

4.2 Variations in Epidote Composition

Studies on compositional variations in epidote have been made mainly under metamorphic conditions (temperature greater than 300°C and pressures generally in excess of 2 kb) (Strens, 1965; Holdaway, 1972; Liou, 1973; Bird and Helgeson, 1980, 1981; Liou et al., 1983). Recently data on epidote mineral chemistry in active and fossil geothermal systems have become available (Muffler and White, 1969; Cavaretta et al., 1983; Shikazono, 1984; Liou et al., 1985, Bird et al., 1984; Lonker et al., 1993; Beaufort et al., 1992; Sveinbjornsdottir, 1992).

The most commonly reported chemical variation in epidote involves changes in Fe^{3+} and Al^{vi} contents. Experimental studies in metamorphic terrains show that the Fe^{3+} contents in epidotes decrease as the oxidation state of the rocks decreases and that epidote becomes more aluminous with increasing temperature (Holdaway, 1972; Liou et al., 1973; Beaufort et al., 1992). In active geothermal fields, a systematic change in the composition of epidote with increasing temperature is observed. There is an overall decrease in Fe^{3+} and a concomitant increase in Al^{3+} and Mg^{2+} (Bird et al., 1988; Beaufort et al., 1992; Bird et al., 1984; Liou et al., 1985).

Despite the large variation within individual samples, average epidote compositions in TGF define a compositional gradient with increasing temperature. Both Si^{4+} and Fe^{3+} cationic abundances show negative correlations with increasing temperature (Figures 2A and 2B) while the tetrahedral Al increases Figure. 2C). The decrease in Si^{4+} with increasing temperature indicates increasing substitution of Al^{iv} for Si^{4+}. The concurrent decrease in Fe^{3+} shows the effect of decreasing fO_2 of the fluid as it rises to the surface.

In contrast to the chlorite in well 5R7D, epidote composition correlates very well with the present-day well temperature. As mentioned before, a temperature reversal has been observed for Well 5R7D. In such situations, deeper samples [e.g. 5R7D/C4 (2504m) and 5R7D/C5 (2587)] would have lower temperatures than samples from the shallower levels. When plotted on Si *vs* T, Fe^{3+} *vs.* T and Al^{vi} *vs.* T diagrams the samples define a pattern similar to those observed in the wells where temperature reversals are not observed. This suggests that *the* 5R7D *epidotes* were formed by the present-day fluid and not relict minerals.

The absence of discontinuous zoning and intergrowths of epidotes of varying composition has been used to support a suggestion that a miscibility *gap* exists between Ps_{13} and Ps_{25} for epidotes formed at lower temperature (Deer et al., 1992). However, epidotes with composition within this composition region are observed in the TGF. A plot of the Ps of TGF epidotes vs. T shows that there exists a continuous range in composition even within *the* supposed miscibility gap.

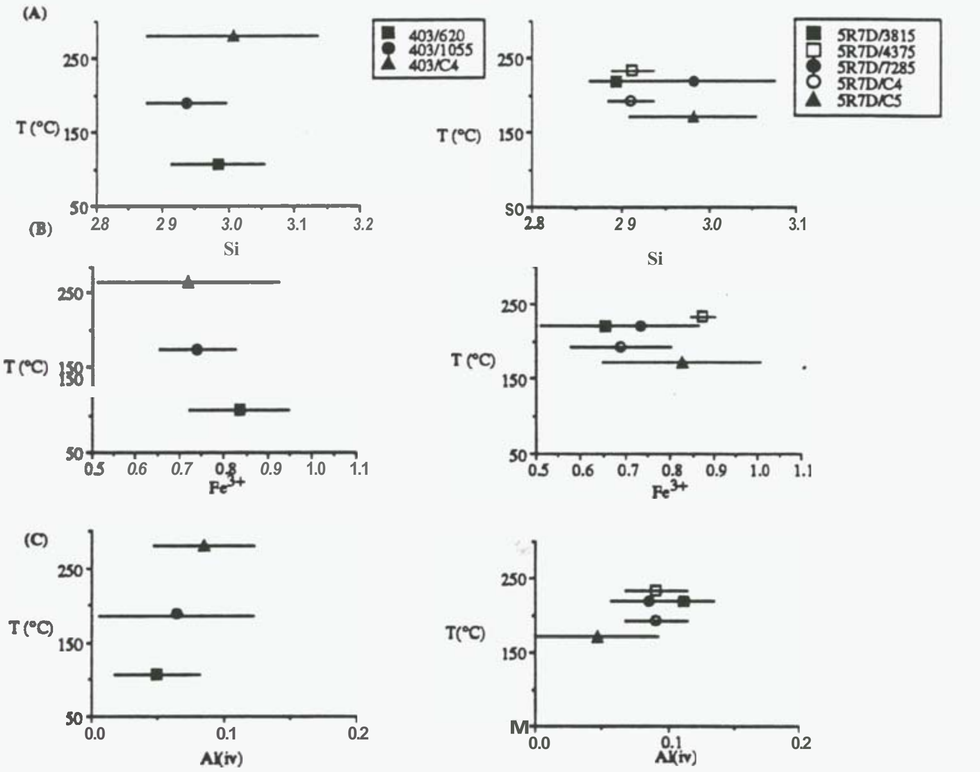

FIGURE 2. Compositional variations in epidotes with measured well temperature. A. Si *vs.* T. B. Fe^{3+} *vs.* T C. Al (iv) *vs.* T.

5.0 CONCLUSION

Chlorite and epidotes in altered andesitic rocks in the Tongonan *Geothermal* Field show compositional changes with temperature and depth. Fe^{2+}, Al^{iv} and Mg abundances in chlorites change systematically with increasing temperature indicating that these chlorites were formed by the present-day fluid. However, some of the samples show negative correlation between these the abundances of these components in chlorites and temperature. This is interpreted to indicate that these chlorites were formed by another fluid which was most likely hotter *than* the presentday fluid. Epidotes show decreasing Fe^{3+} but increasing Al^{iv} with increasing temperature and this is similar to behaviour observed in epidotes from other geothermal areas. Samples from well 5R7D reflect the thermal reversal observed in the well, thus indicating that the epidote found in this well is not a relict mineral but was formed by the present fluid.

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