A COMPARISON OF REE TRENDS IN GEOTHERMAL/ EPITHERMAL SYSTEMS - MODERN AND ANCIENT

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SUMMARY - Rare earth element (REE) behaviour has been studied in hydrothermally altered rocks from four New Zealand geothermal systems (Broadlands, Kawerau, Tauhara and Ohakuri) and compared with two Australian Palaeozoic systems (Mount Aubrey and Conway). The results show that the REE display similar behaviour in geothermal/epithermal systems of different ages. Subparallel REE patterns are characteristic of rocks which are weakly altered or contain a diverse alteration mineralogy, whereas straight trends without Eu anomalies are present in rocks which contain quartz-clay (± albite) assemblages, and bowed trends occur in strongly silicified rocks with minor clay and pyrite. In general, hydrothermally altered rocks display lower REE contents and less pronounced Eu anomalies than fresh rock. REE behaviour during alteration is controlled by alteration intensity, rock permeability, and type of secondary minerals formed. Eu was probably present as Eu^{2+} which accounts for its differential behaviour.

1. INTRODUCTION

Numerous studies conducted on hydrothermal and low-grade metamorphic environments have shown that the REE are mobile to some degree (e.g. Wood et al., 1976; Alderton et al., 1980; Dostal et al., 1982; Taylor and Fryer, 1982; Whitford et al., 1988). However, their behaviour seems to be highly variable due to the complex interplay of many factors e.g. fluid chemistry, primary/secondary mineralogy and fluid temperature (Humphris, 1984). This paper will examine REE behaviour in modern day geothermal systems and compare them to Palaeozoic system with similar alteration styles. As it is possible to directly sample the hydrothermal fluids in active geothermal systems valuable information can be obtained on the relationships between fluid chemistry and REE behaviour. These results may then be applied to Palaeozoic systems and used to explain the observed REE patterns.

2. LOCATION OF THE STUDY AREAS

Figure 1 shows the location of the Mount Aubrey and Conway Palaeozoic epithermal systems from eastern Australia. The Mount Aubrey epithermal gold deposit is situated in the Lachlan Fold Belt approximately 280km WNW of Sydney. It is hosted by a Devonian (?) sequence of intercalated basaltic and andesitic lava flows and minor lithic tuffs. The Conway epithermal gold prospect is located 950km NW of Brisbane in the northern part of the Devonian to Early Carboniferous intracontinental Drummond Basin (Hutton, 1989). The hydrothermal system occurs in Upper Devonian to Lower Carboniferous rhyolitic to basaltic volcanics.

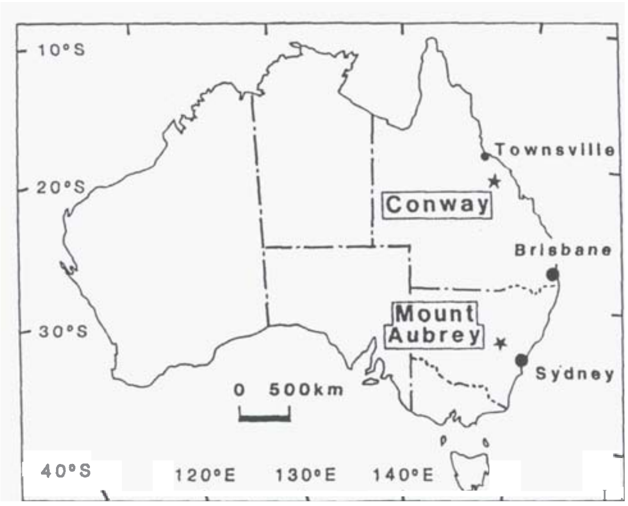

Figure 1- Location of the Mount Aubrey and Conway eastern Australian Palaeozoic epithermal systems

Figure 2 shows the location of the four selected New Zealand geothermal fields in the Taupo Volcanic Zone. The active Kawerau, Tauhara, and Broadlands systems, and the extinct Ohakuri system have been the subject of numerous detailed studies (Browne and Ellis, 1970; Browne, 1971; Henneberger, 1983; Kakimoto, 1983; Browne, 1986; Christenson, 1987; Henneberger and Browne, 1988; Christenson, 1989; Hedenquist, 1990; Lonker et al., 1990). Rhyolitic lavas and tuffs have been selected for REE analysis, mainly due to their dominance in the systems under study, however a small quantity of dacite was also analysed.

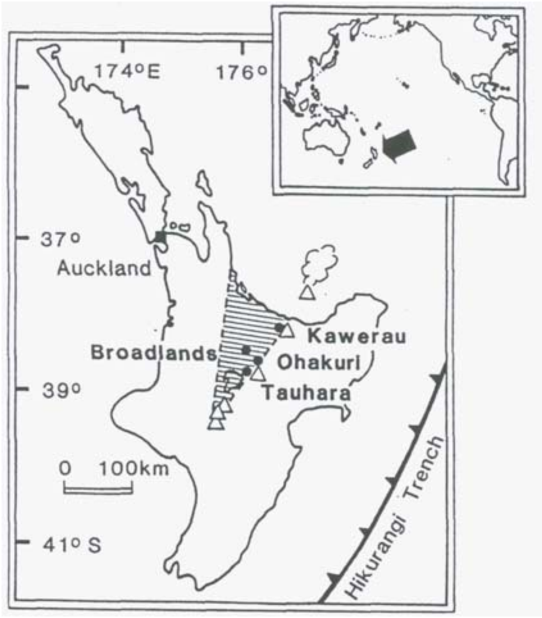

Figure 2- Location of the studied geothermal systems (filled circles) in the Taupo Volcanic Zone (shaded), North Island, New Zealand

3. HYDROTHERMAL ALTERATION IN THE STUDIED SYSTEMS

3.1 Australian Palaeozoic Systems

The Mount Aubrey and Conway areas have been subjected to erosion and hence only a small portion of the original epithermal systems are preserved. In both cases alteration was produced by interaction with alkali chloride fluids. There is no evidence for alteration by acid fluids, either as a result of erosion or because this type of alteration was not developed.

Basalts from Mount Aubrey are relatively fine-grained and display ophitic textures with augite enclosing labradoritic plagioclase phenocrysts (An_{50-65}). The basalts were originally fairly impermeable and hence, are relatively unaltered except in strongly fractured zones. They typically contain secondary albite-chlorite assemblages with minor calcite, epidote, sphene, prehnite, illite and pyrite. All of these phases, with the exception of prehnite, occur as a replacement of igneous phases. Plagioclase is commonly albitised and ferromagnesian minerals are replaced by chlorite and sphene, and less frequently by calcite, epidote and pyrite. Horizons with abundant veining are present in basalt, and vein minerals include bladed calcite, lattice quartz, epidote, albite, illite and pyrite. Andesitic lavas are coarser-grained and porphyritic, and contain zoned plagioclase and minor augite in a finer groundmass of plagioclase laths, and probably, devitrified glass. They are commonly much more intensely altered than basalt, probably due to their higher primary permeability, and contain albite-adularia-clay assemblages ($\pm$ quartz, epidote, illite, apatite, pyrite). Plagioclase is replaced by albite and/or adularia, whereas ferromagnesian minerals are typically chloritised. Epidote, calcite, chlorite, and less frequently, quartz are present as a groundmass replacement.

The temperature and composition of the hydrothermal fluid has been estimated from chlorite thermometry, fluid inclusion data and mineral/fluid equilibria. These methods indicate a temperature of 200-300°C, a salinity of up to 6 equiv. wt percent NaCl, a low f_{CO_2}, and an oxygen fugacity *0.5* to **7** log f_{O_2} units below the hematite-magnetite buffer.

The volcanics from the Conway prospect show a gradational change in composition from basalt at the base of the sequence to rhyolite at the top. Typically, the lavas are porphyritic with a seriate textured groundmass. With the exception of basalt they are strongly altered and display a similar alteration style to that observed in Mount Aubrey. The main alteration phases are quartz, calcite, albite, chlorite, illite, pyrite ($\pm$ adularia, epidote, laumontite). Accessories are allanite and apatite. Calcic plagioclase is commonly albitised, except in basalt, and mafic phenocrysts are pseudomorphously replaced by chlorite. The conditions of hydrothermal alteration have been estimated by using the stability of secondary phases and vein assemblages. The vein mineralogy (abundant calcite with little epidote) indicates that f_{CO_2} was relatively high, and the mineral paragenesis indicates a fluid temperature of at least *250°C.*

3.2 New Zealand Samples

The majority of the New Zealand samples have been altered by near neutral chloride fluids resulting in the formation of secondary albite, adularia, quartz, calcite, chlorite, epidote, zeolites (e.g., wairakite and laumontite), pyrite, illite, montmorillonite and mixed layer clays.

A small proportion of the samples have been altered by acid fluids and contain alteration assemblages typical of acid sulfate steam condensates. Secondary minerals in these rocks include kaolinite, alunite, cristobalite, opal and quartz.

4. RESULTS: REE TRENDS FROM HYDROTHERMALLY ALTERED ROCKS

REE analyses were carried out by instrumental neutron activation on 1g of sample powder. The raw REE concentrations were converted to mg/1000cc to take into account density changes during alteration. The analyses were then chondrite-normalised using data from Boynton (1984), and rock-normalised using the average composition of the least altered equivalent lava from each system.

4.1 New Zealand Geothermal Systems

REE patterns of unaltered rhyolite are characterised by moderately steep negative slopes (mean $(La/Lu)_{cn} = 4.81$) and distinct negative Eu anomalies ($(Eu/Eu^*)_{cn} = 0.47$-0.65) (Fig. 3).

REE contents of altered rocks are depleted relative to the least altered sample and the negative Eu anomaly is less pronounced. The REE trends can be placed in three main groups (subparallel, flat and bowed trends) regardless of whether the samples were altered by acid or alkaline chloride fluids. Some unusual trends have been observed in

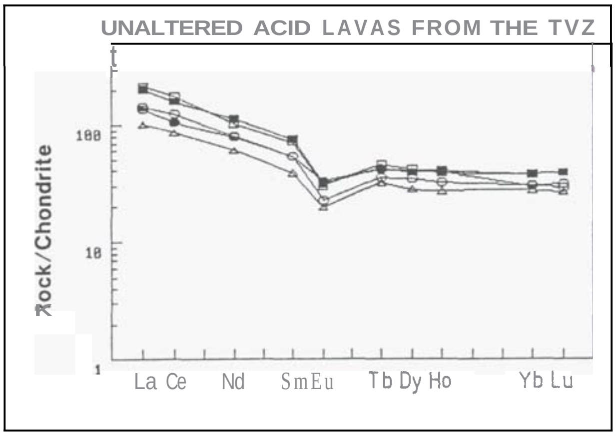

Figure 3- SG-corrected REE trends of unaltered and least **altered** rhyolites **from** the Taupo Volcanic **Zone**

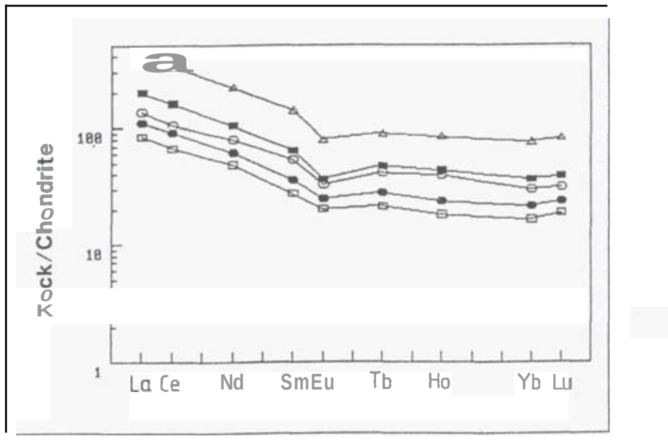

Figure 4- Subparallel **SG-corrected** trends displayed by samples with diverse **secondary** assemblages. ***An*** illite-rich sample **(open** triangles) shows REE enrichment relative to least altered rhyolite

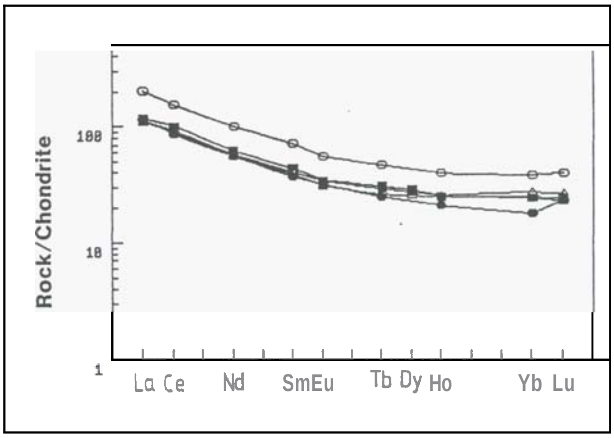

Figure **5A-** Flat SG-corrected chondrite-normalised patterns

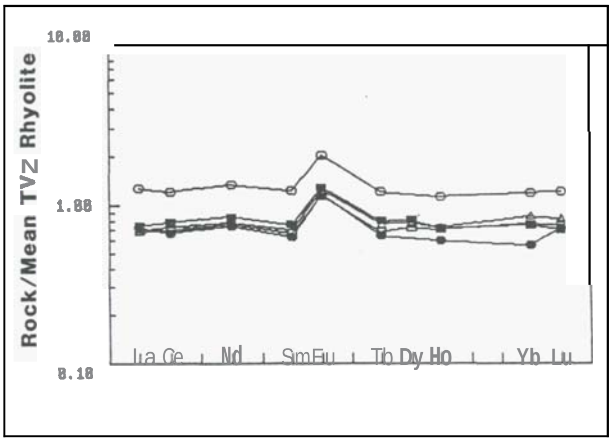

Figure 5B- SG-corrected rhyolite-normalid trends showing positive Eu anomalies

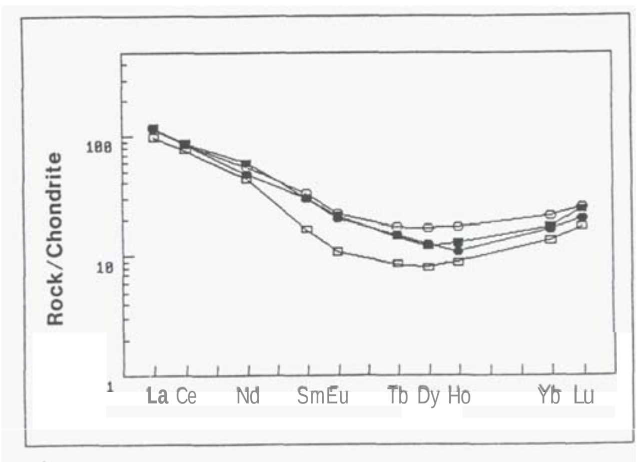

Figure 6- Bowed SG-corrected trends of samples containing **quartz** $\pm$ clay, pyrite assemblages

rocks **that** are very strongly altered by acid fluids, however **these** trends **are** not **common.** Subparallel trends are **shifted** vertically relative to the least altered sample, and commonly lie below the field defined by fresh rhyolite, with the exception of an illite-rich sample (Fig. **4).** These trends are present in samples which contain a diverse **secondary** assemblage (clay, **quartz,** albite, adularia, calcite, chlorite, $\pm$ zeolites, epidote, sphene, opaques) and/or which are weakly altered and have relict igneous textures. Flat REE trends with **no** Eu anomaly are displayed by samples with quartz-chlorite and quartz-clay-zeolite assemblages (Fig. 5A). Rock-normalid plots of these analyses show addition of Eu, whereas the rest of the REE have remained relatively immobile (Fig. 5B). Strongly silicified samples ($\pm$ clay, pyrite) typically exhibit bowed curves due to a depletion of the light HREE such **as** Ho, Tb **and** Dy (Fig. 6).

4.2 Australian Palaeozoic Epithermal Systems.

Least altered basalt from the Mount Aubrey deposit typically exhibits flat REE patterns ($(La/Lu)_{cn}$ = **2.94)** with weak negative Eu anomalies **($(Eu/Eu^*)_{cn}$** = 0.82). The least altered andesitic lavas have higher total REE contents, show stronger fractionation of the LREE from the HREE ($(La/Lu)_{cn} = 6.46$), and display more distinct negative Eu anomalies ($(Eu/Eu^*)_{cn} = 0.60$) (Fig. 7).

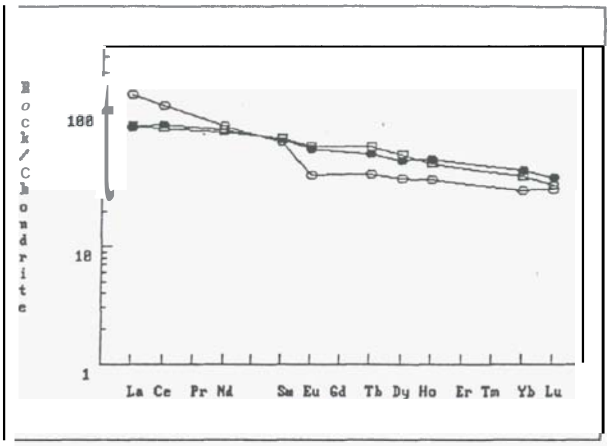

Figure 7- REE patterns of the least altered andesitic (open circles) and basaltic lavas (filled circles and open squares) from Mount Aubrey

Basalts from the Mount Aubrey system which contain diverse secondary assemblages (albite, chlorite, epidote, sphene) characteristically exhibit subparallel trends (Fig. 8). A negative Eu anomaly is absent because it is very small in least altered basalt and only a slight addition of Eu is necessary to cause the anomaly to disappear. The andesites display subparallel and flat trends which are more noticeably displaced from the least altered rock (Fig. 9). Subparallel trends are typically present in samples with chlorite, albite, mixed layer clay and calcite assemblages (± adularia, illite, epidote, quartz, apatite, pyrite), whereas flat trends occur in samples which contain quartz, chlorite, albite and epidote.

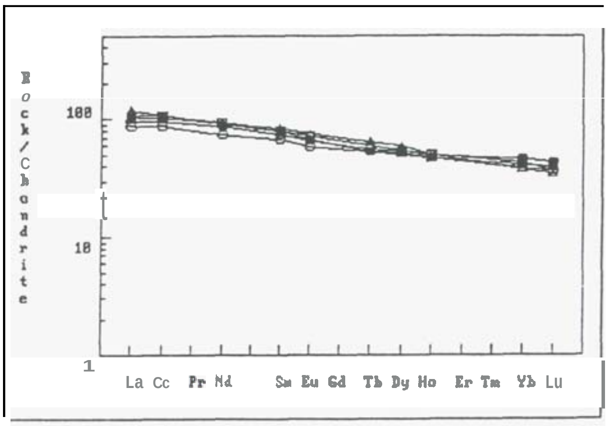

Figure 8- Subparallel SG-corrected trends of altered basalt from Mount Aubrey

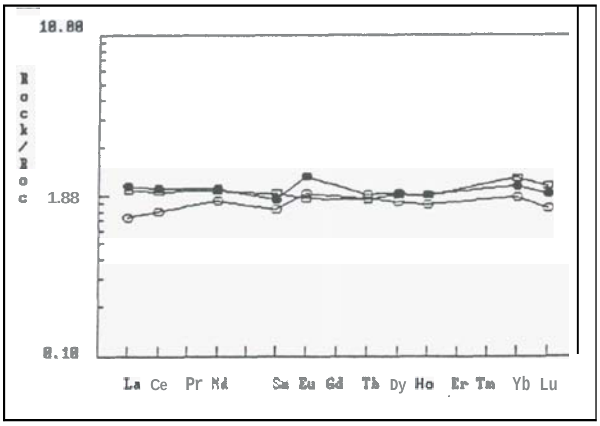

Figure 9- Rock-normalised subparallel trends (open circles and open squares) and flat trends with distinct Eu anomalies (filled squares), in altered andesite from Mount Aubrey

In the least altered lavas from the Conway prospect the degree of LREE to HREE fractionation and the size of the negative Eu anomaly increases from basaltic through to rhyolitic lavas (Fig. 10). If these lavas are cogenetic then the REE ratios should be consistent throughout the series, e.g. the REE would gradually become more enriched and the size of the negative Eu anomaly would progressively increase in the more acid members of the series (Cox et al., 1979). From the REE trends it is not obvious if these lavas are cogenetic. Furthermore, the trends may not truly reflect the primary REE composition of the rocks because of the effects of alteration, especially in the more intermediate to acid lavas.

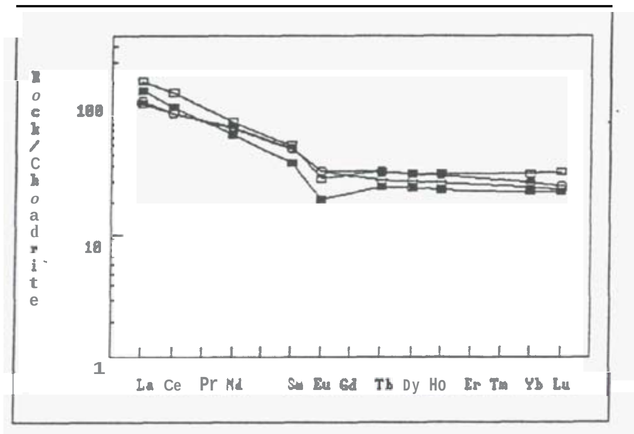

Figure 10- REE composition of the least altered lavas from the Conway prospect; basalt = open and filled circles; intermediate lava = open squares; rhyolite = filled squares

Altered basaltic, intermediate and rhyolitic lavas from Conway which contain diverse alteration assemblages (chlorite + albite + adularia + quartz + sphene + calcite) typically display subparallel trends with weaker negative Eu anomalies. In contrast, intermediate lavas with quartz and clay ± calcite assemblages characteristically exhibit flat trends without Eu anomalies. The degree of depletion of the REE in altered samples is generally grater in samples with higher silica contents. Because of the possibility that the Conway lavas may represent a fractional crystallisation series, it could be argued that subparallel REE trends are the result of fractionation. However, this cannot account for the disappearance of the Eu anomaly in altered rocks, especially in the more acid lavas, therefore it is suggested that the shift in REE patterns is due at least in part to hydrothermal alteration.

Typically, vein fillings (quartz, calcite) from Mount Aubrey and Conway are characterised by very low REE concentrations and REE trends which differ markedly from those of their hosts.

5. DISCUSSION

REE behaviour in altered rocks from the Australian Palaeozoic systems is remarkably similar to that observed in the active New Zealand systems. Altered rocks display lower total REE contents and less distinct negative Eu anomalies. The types of REE patterns common to both environments include subparallel and straight patterns without Eu anomalies. Bowed trends were only observed in strongly silicified samples from New Zealand.

Subparallel trends are characteristic of rocks which contain a wide variety of secondary phases including epidote and/or albite. These assemblages suggest a low permeability, and hence low fluid/rock ratios (Browne, 1978). It is concluded that the degree of REE depletion may be correlated with fluid flux. Conversely, rocks with one dominant alteration phase (e.g. quartz) display bowed trends which differ markedly from the least altered rock. This suggests that the REE *can* be accommodated in the rock where a diverse secondary assemblage is present, whereas in samples with one dominant alteration phase it is more probable that not all REE will be retained in the altered rock. High fluid/rock ratios and/or higher primary permeability may account for the bowed trends of strongly silicified samples.

Eu is considered to be mobile because of the reduction in size of the negative Eu anomaly in altered samples. The differential behaviour of Eu relative to the other REE indicates that Eu^{2+} was the stable species in the hydrothermal fluids (200-300°C). Eu^{2+} will be liberated when igneous plagioclase is altered and may be accommodated where suitable hosts are present. In the samples from New Zealand and Australia, flat chondrite-normalised trends are displayed by samples which contain mainly clays, chlorite and zeolites, suggesting that these minerals are capable of fixing Eu^{2+}. It is suggested that in New Zealand part of the Eu^{2+} added during alteration may have originated from the underlying greywacke basement, which contains igneous fragments with abundant plagioclase (Ewart and Stipp, 1968), as none of the analysed samples showed an increased negative Eu anomaly as might be expected if Eu was simply redistributed. Furthermore, the size of the Eu anomaly appears to be related to rock permeability and hence Eu may be an indicator of fluid flux. In the Mount Aubrey samples, flat trends without Eu anomalies are only present in the more permeable intermediate lavas, and not in basaltic lavas with comparable secondary assemblages.

6. CONCLUSIONS

REE trends of altered rocks from geothermal/epithermal systems of various ages are consistent and they show that the REE are mobilised during hydrothermal alteration. The degree of REE depletion depends largely on secondary mineralogy and fluid/rock ratios. In rocks with a variety of secondary phases the REE are more likely to be retained. Altered rocks typically display a reduced negative Eu anomaly due to the addition of Eu. This differential behaviour of Eu compared to the rest of the REE is probably due to its presence as Eu^{2+}. Eu is especially enriched where suitable host minerals are present (e.g. clays, chlorite, zeolites).

7. ACKNOWLEDGMENTS

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