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Rare earth element systematics of acidic geothermal waters from the Taupo Volcanic Zone, New Zealand

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Abstract

Concentrations of rare earth elements (REE) in acidic thermal waters from the Taupo Volcanic Zone, New Zealand have been determined. Acidity in waters from Rotokawa results from oxidation of H_2S upon encounter with oxygen-rich meteoric waters. The Ruapehu Crater lake is acidic due to input of magmatic volatiles such as HCl and SO_2. REE concentrations in both types of water are high, ranging from 10^{-3} to nearly 1 times chondrite. Chondrite-normalized patterns for heavy REE in waters from Rotokawa parallel those of their host rocks, suggesting little fractionation upon water–rock interaction. However, the light REE are depleted relative to their host rock, resulting in a "gull-wing" pattern. The hyperacidic Ruapehu Crater lake water generally does not have a "gull-wing" pattern. The patterns for these waters were invariant for several years prior to the September 1995 eruption, but changed substantially afterwards, generally decreasing in slope with time.

Keywords: Rare earth elements; Acidic geothermal waters; Taupo Volcanic Zone, New Zealand

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1. Introduction

Measurement of the concentrations of rare earth elements (REE) in geothermal fluids may provide important clues to the nature of water–rock interaction in geothermal systems. Only relatively recently have such data become available for continental geothermal systems (e.g., Lewis et al., 1997; van Middlesworth and Wood, 1998; Wood, 2003). However, considerably more research is required before the REE can be used routinely as tracers in geothermal systems. In this paper, REE data for low-pH thermal springs from Rotokawa and the Mount Ruapehu crater lake, both located in the Taupo Volcanic Zone of New Zealand, are reported for the first time.

2. Methods

At Rotokawa, two 1-l samples were taken from each of three acid-sulfate springs. At each spring, one liter was acidified directly (unfiltered) and the other liter was passed through a 0.45-μm filter (filtered). At Mount Ruapehu, only unfiltered samples were taken. All samples were analyzed for REE by ICP-MS, either directly or after suitable dilution. Conditions of analysis were adjusted to minimize isobaric interferences, but corrections were necessary for interference by BaO on Eu.

3. Results and discussion

Lake Rotokawa is an acidic lake fed by numerous thermal springs and the site of a recently developed geothermal power station. We report REE analyses for

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three springs (samples taken in March 2000) from the area, all of which have low pH (1.5–2.8) and moderately high chloride and sulfate. At Rotokawa the acidity is primarily a result of oxidation of H_2S, released to the vapor during vapor–liquid phase separation of a deep reservoir fluid, to form H_2SO_4 upon contact with oxygen in shallow meteoric water (Krupp and Seward, 1987). The low-pH geothermal fluids from Rotokawa exhibit relatively high REE contents (mostly 10^{-3} to 10^{-1} times chondrite) and the filtered aliquots of the various samples have nearly identical REE concentrations to those of the unfiltered aliquots, suggesting that the REE are present in true solution or as very fine colloids (Fig. 1).

The chondrite-normalized patterns for the low-pH waters from Rotokawa have a very distinctive “gull-wing” pattern in which there is a small but noticeable negative Eu anomaly (the gull body), and light (La–Sm) and heavy (Gd–Lu) “wings”. The heavy REE wings are more or less parallel to the patterns of local host rocks (TVZ rhyolites), but the light REE wings exhibit depletion of the lightest REE (La–Nd) compared to host rocks. Although the overall patterns for the waters have negative slopes, the lightest REE portions have positive slopes. Although it is hard to tell because Gd data are absent for the TVZ rhyolites, the negative Eu anomaly in the waters appears to simply reflect a negative Eu anomaly in the host rocks. Similar “gull-wing” patterns have been observed in many other acid-sulfate geothermal fluids in New Zealand (e.g., Waiotapu, Orakeikorako) and elsewhere, and appear to be characteristic of shallow acid-sulfate systems (Wood, 2003). The reason for the depletion in the light REE relative to the host rock is not yet known.

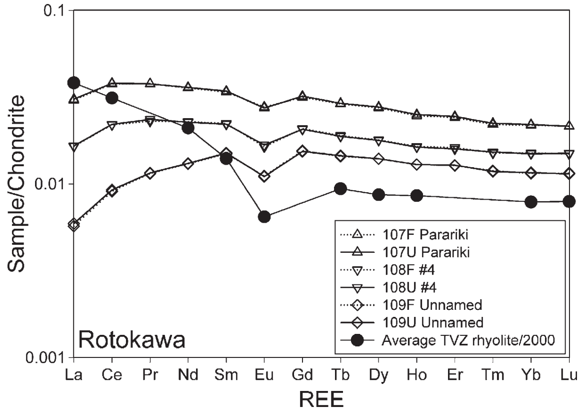

Fig. 1. Chondrite-normalized REE patterns for acid-sulfate waters from Rotokawa. Data for unfiltered samples are connected by solid lines and those for filtered samples by dotted lines. Chondrite values are from Boynton (1984). Average rhyolite composition is taken from Hopf (1993).

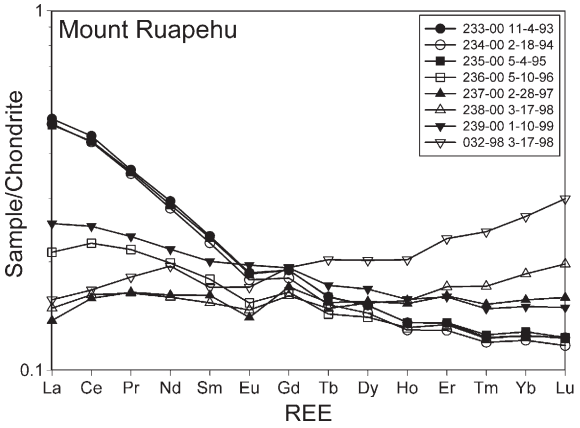

Fig. 2. Chondrite-normalized REE patterns for water from the crater lake at Mount Ruapehu as a function of time. Chondrite values are from Boynton (1984).

The fluid from the crater lake at Mount Ruapehu is an acid–chloride-sulfate water (pH 1.14 in 1998) with extremely high dissolved solids contents, including Mg, Ca, Na, Fe, and Al, each at concentrations greater than 1000 mg/L. In contrast to the system at Rotokawa, the acidity of the Mount Ruapehu crater lake is a result of the direct input of acidic magmatic volatiles such as HCl and SO_2 (Christenson, 2000). A liter of unfiltered water was obtained from Ruapehu crater lake by Bruce Christenson in March 1998 and analyzed by us within a few months for REE. In addition, a series of unfiltered samples, taken from Mount Ruapehu between 1993 and 1999, inclusively, and stored in the sample library at the Institute of Geological and Nuclear Sciences (IGNS) at Wairakei, were analyzed in 2000. These samples permit an examination of changes in the REE geochemistry during a period of time spanning an eruption of Mount Ruapehu.

Eruptive activity at Ruapehu started in September 1995 after a period of relative quiescence, and continued for approximately one year afterwards. The lake was expulsed by the September and October eruptions, but it began to return by mid-November (Christenson, 2000). Data reported by Christenson (2000) show systematic changes in chloride/sulfate ratios, and the concentrations of many metals, including Mg, Al, and Fe, in the lake prior to and after the eruption. Christenson (2000) interpreted the changes in water composition to result from magma degassing combined with dissolution of andesitic magma during the eruption.

The concentrations of the REE in the Ruapehu crater lake are extremely high, ranging between 10^{-1} and 1 times chondrite. Although only unfiltered aliquots are available from Mount Ruapehu, the very low pH permits the assumption that filtered aliquots would have identical REE concentrations, in analogy with the acidic fluids from Rotokawa.

The REE patterns of samples from the crater lake at Mount Ruapehu are different from most of the other acidic fluids sampled from New Zealand in that they generally do not have a "gull-wing" chondrite-normalized REE pattern (Fig. 2). This is especially the case for the pre-eruption samples. However, some of the post-eruption samples do have "gull-wing" patterns. It is interesting that the chondrite-normalized REE pattern for a sample taken in March 1997 from the Copahue crater lake (pH 0.18 to 0.30) in Argentina (see Gammons et al., 2005) also does not have a "gull-wing" appearance. In particular, the hyperacidic waters from these crater lakes do not appear to show consistently the depletion in the light REE relative to host rock that is so common in the somewhat less acidic waters derived from oxidation of H_2S (e.g., Rotokawa). It may be that below a certain critical pH ($<1.5–2$), crater lake waters acquire REE from rock or magma with little fractionation across the entire series, whereas waters with pH in the range 2–4 tend to fractionate the light REE.

Like the major cations and anions, the REE compositions show a distinct evolution related to the September 1995 eruption. Three samples taken prior to the initiation of eruptive activity in September 1995 exhibit nearly identical, negatively sloped, chondrite-normalized patterns (Fig. 2). In the samples from 1996 to 1998, the overall REE patterns first flatten and then become slightly positively sloped. In 1999 the water pattern again became slightly negatively sloped.

According to the data reported by Christenson (2000), elements such as Al, Fe, Mg and Na already showed substantial changes in May 1995 compared to their 1994 levels. However, the REE concentrations in November 1993, February 1994 and May 1995 were nearly identical. Although there are not as many samples for the REE as a function of time, it appears that REE concentrations did not change until during or after the September eruption. If this is the case, then the REE may not be as sensitive indicators of impending eruptive activity as some other elements appear to be.

The possibility that the IGNS samples might have changed during storage cannot be discounted entirely. However, some measure of the magnitude of this potential problem is given by comparison of sample 032-98 with sample 238-00. These represent two different aliquots of the sample procured by Christenson in 1998, but sample 238-00 was stored for more than two years in the IGNS sample library prior to analysis. It can be seen from Fig. 2 that the two aliquots have essentially identical LREE concentrations, and the HREE concentrations differ by less than a factor of two. This finding suggests that the samples did not change significantly over a period of two years. Moreover, if changes during storage had significantly affected these samples, it would be highly fortuitous that the three oldest samples would have nearly identical REE patterns, but that a significant change in these patterns happened to occur only in samples procured after the eruption.

4. Conclusions

Low-pH geothermal fluids are capable of carrying significant quantities of REE ($>10^{-3}$ times chondrite), and most of the REE load is probably present in true solution or as fine colloids. Acid-sulfate waters that gain their acidity via the oxidation of H_2S at shallow levels have a distinctive "gull-wing" chondrite-normalized pattern with a negative Eu anomaly (the gull body), and heavy and light REE "wings". The heavy REE portion of the pattern parallels that of the host rock, whereas the light REE are depleted, often substantially, relative to the host rock. On the other hand, waters from hyperacidic volcanic craters, where acidity is introduced by acidic magmatic volatiles, do not consistently exhibit these "gull-wing" REE patterns. The higher acidity of the crater lake waters compared to those at Rotokawa, for example, may result in host-rock or magma dissolution with minimal REE fractionation, at least during some periods of evolution of the system. The REE patterns of crater lake waters reflect changes that occur in the magmatic system associated with eruptions, and may represent an additional tool to help understand the processes occurring in magma chambers during eruptions.

Acknowledgements

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