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PRELIMINARY MEASUREMENTS OF CONCENTRATIONS OF LANTHANIDE ELEMENTS IN GEOTHERMAL FLUIDS FROM THE TAUPO VOLCANIC ZONE, NEW ZEALAND

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ABSTRACT

Measurement of the concentrations of rare earth elements (REE) in geothermal fluids and associated altered rocks holds promise as a potential aid in exploration for and exploitation of geothermal fields of economic importance. We have initiated a research program which will provide the basis for assessing this potential. The project involves measuring the REE content of fluids from a variety of geothermal systems from around the world and relating measured contents to such parameters as fluid chemistry and the type of rock through which the fluid flows. The overall objectives of the research are to: 1) establish baseline information on REE contents in geothermal fluids from around the world; 2) determine whether there are any distinctions in REE contents of fluids from producing or potentially producing geothermal fields, and geothermal fields which are not economically viable; 3) establish any relationships between REE contents and fluid chemistry and temperature which may exist; 4) establish relationships between REE contents and host (aquifer) rocks; 5) determine whether there are seasonal changes in REE geochemistry of geothermal fluids; and 6) ascertain whether REE geochemistry changes systematically over the production history of a producing geothermal field.

Our methodology is to collect both filtered and unfiltered samples preserved with 2% high-purity acid in acid-cleaned bottles. Temperature, conductivity, and pH are measured in the field. Alkalinity, selected anions and cations, and silica are measured in the laboratory. The REE's, Th, and U are determined after a preconcentration step involving addition of about 60 mg ferric iron to the preserved sample followed by addition of high-purity ammonia which precipitates the iron as ferric hydroxide and co-precipitates the REE's, Th, and U. The sample is filtered to recover the precipitate which is then redissolved in high purity acid and analyzed by ICP-Mass Spectroscopy. We have demonstrated sample detection limits better than of 0.01 μg/L or 0.05 nmole/Kg for most of the REE's, Th and U.

We present preliminary results from geothermal areas in and around the Taupo Volcanic Zone, New Zealand. Low-pH, acid-sulfate geothermal fluids have been found to have elevated, light REE-enriched patterns while geothermal fluids having near neutral and higher pH have much lower REE contents.

COLLECTION OF THE SAMPLES

These samples were collected in March of 1998 and analyzed at facilities at the University of Idaho and Washington State University. The methodology is modified after that developed by van Middlesworth and Wood (1998). Before going out into the field, High Density Polyethylene (HDPE) bottles for containing acidified metal samples were cleaned by soaking overnight in 10% nitric acid. Bottles for anion and silica samples were soaked in deionized water (DIW) overnight. All bottles were then rinsed at least three times with DIW. Sediments and suspended solids were excluded from the cation, anion, and silica samples. For the New Zealand samples this was accomplished by decanting the aliquot for analysis after allowing the well mixed sample to settle for a few days. All subsequent samples are now filtered in the field directly from a designated sampling bottle into the appropriate sample containers. At each site the following fluid samples were taken:

1) a 1-liter, filtered sample (filtered using a 0.45 μm membrane), preserved with 2% Seastar Baseline HNO_3 for REE analysis
2) a 1-liter, unfiltered sample, preserved with 2% Seastar Baseline HNO_3 for REE analysis
3) a 250-mL unfiltered sample, preserved with 1% trace metal grade HNO_3 decanted later for alkali, alkaline earth and transition metal analyses

4) a 250-mL unfiltered sample decanted later for anion analysis and alkalinity determinations
5) a 5 mL unfiltered sample diluted with 50 mL of DIW for silica analysis

The following measurements were made in the field at each site: temperature, conductivity, pH, Eh and alkalinity. Except for samples from geothermal wells, pH, Eh and conductivity determinations were made at, or as close as possible to, the emergence temperature of the fluid. The pH and Eh buffers used to calibrate the respective electrodes were also maintained at as close to the emergence temperature of the fluids as possible. Alkalinity measurements were made within a week of sample collection using an automatic titrator at IGNS in Taupo.

Location and Description of Samples

The sites selected for sampling are located on the north island of New Zealand. Two sites, Miranda and Te Aroha were selected because they are thought to result from circulation of fluids along deep regional faults, where heating is predominately derived from the geothermal gradient as opposed to the shallower circulation typical of most of the thermal areas in the Taupo Volcanic Zone (TVZ), where heating is dominated by subvolcanic sources. Two other sites, Morere and Te Puia, outside of the TVZ proper, were sampled because they are associated with dewatering of sediments accompanying the Pacific plate, which is being subducted underneath the Indian plate just off the eastern coast of the North Island of New Zealand. Nine thermal areas within the Taupo Volcanic Zone were sampled; Waimangu, Waiotapu, Waikite, Te Kopia, Orakeikorako, Broadlands-Ohaaki, Rotokawa, Wairakei, and Tauhara-Taupo. Waikite, Te Kopia, and Orakeikorako are associated with faults (Simmons 1995). Waimangu, Wairakei, and Taupo-Tauhara are associated with caldera boundaries (Simmons 1995).

Waiotapu Thermal Reserve

The Waiotapu Reserve contains the largest chloride spring in the region (the Champagne Pool) and a number of acid sulfate springs. We sampled the outlet of the Oyster pool which is fed by the outflow of Champagne pool and a number of smaller springs. Also sampled was a small hot spring feeding directly into the pool below the Oyster pool at the end of the Oyster pool side trail. The Oyster pool springs are strongly acidic with moderately high conductivity. The Champagne Pool was sampled as the definitive chloride feature in this reserve. The Champagne Pool has very high conductivity and has a low Eh as demonstrated by the As, Sb, and ferrous iron sulfide precipitation on the margins of the pool. Field measurements and elevation differences between different pools in this reserve make it clear that the underlying plumbing systems are capable of producing relatively isolated water chemistries from the same system. This area has a high maximum deep temperature of 295°C as well as high heat flow of 600 MW with an estimated thermal reserve of 6100 PJ. Surface water flow is greater than 250 L/s (Mongillo and McClelland, 1984).

Te Kopia Reserve

The Te Kopia Reserve is comprised of three large pools fed by acid sulfate springs. The northernmost pool is horseshoe-shaped and was sampled at the north end of the inner peninsula. The southern pool was sampled at the southern margin near active inflow from submerged springs. A final sample was obtained from a small active spring at the Paeroa fault scarp. All of the samples were strongly acidic with pH ranging from 2.61 to 1.74, and Eh determinations indicated relatively oxidizing fluids. Estimated deep temperature maxima are 241°C with an estimated thermal reserve of 2300 PJ (Mongillo and McClelland, 1984).

Miranda hot springs

The Miranda hot springs were sampled because they are heated entirely by the geothermal gradient along a very deep-seated fault system not directly related to magmatic intrusions. The rationale for sampling this type of feature is that there might be significant differences between deeply circulating meteoric waters in contrast to waters that may have a magmatic input. The Miranda springs flow at a rate of up to 7 L/s (Mongillo and McClelland, 1984). Field measurements indicate low conductivity and a slightly basic pH of 9.1.

Te Aroha

The Te Aroha hot springs are a second example of deep circulating meteoric waters heated entirely by the geothermal gradient along deep-seated faults. These waters were quite different from Miranda hot springs in that the Te Aroha waters have unusually high bicarbonate contents and conductivities and near neutral pH ranging from 6.9 to 7.8. We took samples from Mokena Geyser, which is a drillhole, 70 meters deep (drillhole #1; Mongillo and McClelland, 1984), a cold spring (spring #8; Mongillo and McClelland, 1984), and a hand-pumped well containing thermal fluid (spring #15; Mongillo and McClelland, 1984).

Waimangu

The Waimangu area is similar to Waiotapu in that it comprises both acid-sulfate features and neutral-chloride features. This hydrothermal system occurs

along the southern margin of the Okataina Volcanic Center. The heat source seems to be related to the central rift zone of a nearby volcanic edifice. This volcanic center is the most recently active one in the TVZ. The maximum deep temperature is estimated to be 270°C with stored heat estimated to be 5400 PJ (Mongillo and McClelland, 1984). Samples were obtained from the acidic Frying Pan lake, as well as the neutral-chloride Clamshell Spring and Iodine Pool. In the latter, a replicate sample was taken to test the homogeneity of the Pool and the reproducibility of our analytical results.

Orakeikorako Field

The Orakeikorako field is reached by a short ferry trip across the east end of lake Ohakuri on the Waikato river. The sinter terrace system produced by the flow of springs is quite large and mostly lies beneath the present lake level. The samples are neutral to slightly basic and slightly reducing. Field conductivity measurements suggest that total dissolved solids content is low, which is in agreement with published data on the field. Temperature at depth is estimated to be 266°C with a stored heat reserve of 1700 PJ (Mongillo and McClelland, 1984).

Waikite

The Waikite hot springs lie to the north of the Te Kopia Reserve field along the Paeroa fault zone. Part of the waters of Waikite hot springs are diverted to a wading pool. Sampling was done within the fenced off area at the north end of the parking lot from a weirbox built around the natural spring. The Waikite hot spring has a higher temperature, approximately neutral pH, and slightly reducing Eh in contrast with the acidic, strongly oxidizing, Te Kopia Reserve waters. Waikite is proximal (~5Km) to Waiotapu and may have a hydrological connection to the Waiotapu field (Mongillo and McClelland, 1984). The sampling of Waikite was immediately followed by a magnitude 4.1 earthquake which had an epicenter at nearby Rotorua. The proprietor of the Waikite springs indicated that earthquakes in the general area are periodic in that activity increases for a few weeks at a time followed by several months of little or no activity. This was confirmed by discussion with our colleagues at IGNS. We did not ascertain whether these quakes cause movement along the Paeroa fault zone. Seismicity may be significant because Lewis et al. (1997) have attributed temporal variations in REE contents in Yellowstone National Park to microseismic events.

Rotokawa

Rotokawa (Maori for bitter lake) is an acidic lake fed by numerous springs. We were able to sample two surface springs. The area contains abundant elemental sulfur deposits. The acid spring waters made access dangerous because of dissolution and undermining of ground near the springs and in the general area. Deep temperatures and stored heat have been estimated at 335°C and 4500 PJ, respectively (Mongillo and McClelland, 1984).

Morere

The Morere springs are neutral-chloride waters thought to be derived from dewatering of the sedimentary wedge of the underlying subduction zone. These springs had very high conductivity, neutral-chloride waters. In addition, the waters were clearly high in iron and were precipitating iron hydroxides upon emergence at the surface.

Te Puia

Like the Morere springs, The Te Puia springs may be derived from dewatering of the underlying subducted slab. Field measurements of the waters indicated high conductivity, neutral pH, and reducing Eh which seemed to be precipitating sulfur. Abundant calcite veins and surface crystals seems to indicate that the waters are calcite-saturated. There is a strong presence of natural gas in the area, suggesting that these waters may interact with organic matter at depth.

Wairakei Field deep wells

The Wairakei fields are famous as the first liquid-phase geothermal field to produce electric power. A number of geothermal production technologies were developed for the first time at Wairakei. Samples were obtained from two wells. Well #229 was sampled from the weirbox and the high pressure wellhead with a Weber sampler to make possible the comparison of REE contents at the wellhead and directly after production. A second well was sampled at atmospheric pressure from a drain point downflow of the wellhead. The field measurements indicate slightly basic pH and moderate conductivity. Downhole temperature maxima are approximately 270°C; total heat flow is estimated to be 600 MW with a stored capacity of 6700 PJ (Mongillo and McClelland, 1984).

Broadlands-Ohaaki Field deep wells

Three wells were sampled at Broadlands-Ohaaki. Again, one was a sample at atmospheric pressure downflow from the wellhead. Two others were taken from high-pressure wells using the Weber sampler. Field measurements indicate moderate conductivities,

slightly basic pH, and reducing Eh. Downhole temperature maxima are approximately 308°C with a stored capacity of 6900 PJ (Mongillo and McClelland, 1984). Few surface springs existed prior to field development and surface heat flow is estimated to be 75 MW (Mongillo and McClelland, 1984).

Tauhara-Taupo Field; De Bretts Thermal Park

The Tauhara-Taupo field contains both acid-sulfate and neutral-chloride features but we were able to sample only one thermal spring within the De Bretts thermal park. Field measurements indicate that the spring has near neutral pH and relatively low conductivity.

Mt. Ruapehu crater lake

The sample (NZ-032-98) was taken from Ruapehu crater lake by Bruce Christenson. Sample preservation was not a problem because the lake is strongly acidic (pH = 1.14). Only one liter of unfiltered sample was obtained because of logistical difficulties.

ANALYTICAL METHODS

The methodology for the REE was complicated by the difficulty of finding a filter medium that has a low blank value and is also capable of collecting ferric hydroxide precipitate without immediately clogging. Previously employed membrane filters were found to be unsuitable for the large number of samples in this study as they clogged too quickly, reducing the rate of filtration and causing a serious bottleneck in sample processing. Borosilicate glass-fiber filters have a very high blank for Sc, Y, Zr, REE's, Th, and U and in addition are essentially uncleanable. Quartz-fiber filters have been found that have adequate blank values after a cleaning procedure followed by minimization of exposure time to the filter media. Two procedural variations and two filter sizes were tried. Method detection limits were established for each variation. The best method will be described below.

Quartz-fiber filters are prewashed by assembling the filtration apparatus and aspirating two or more successive aliquots of hot 50% aqua regia through a stack of a dozen filters. This is followed by rinsing with deionized water. The cleaned filters are allowed to dry in a clean enclosed container for later use.

The REE's are concentrated for analysis by addition of ferric iron to the sample container such that the final concentration of ferric iron in the sample is about 60 mg/L (ppm). A 50-mL aliquot of each REE sample was saved for direct analysis in case a more sensitive ICP-MS (which would obviate the need for sample preconcentration) becomes available in the future. The remaining sample is weighed to determine the concentration factor and 50 mL of 22% trace metal grade ammonia are added to neutralize the 2% acid and raise the pH to between 8 and 9. The sample is mixed and a pronounced color change is observed as the iron precipitates as a gelatinous flocculate. The sample is allowed to stand for at least an hour and the reddish ferric hydroxide precipitate settles to the bottom of the sample bottle.

The next step is vacuum-filtration of the sample through a 55- to 90-mm quartz-fiber filter. The filter assembly is prewashed and soaked in an acid bath then rinsed with DIW immediately prior to filtration. The apparatus is assembled and rinsed successively with 10% (v/v) trace-metal-grade hydrochloric acid solution, DIW, and finally a 2% solution of trace-metal-grade ammonia to remove all traces of acid. The filtrate is discarded and the sample filtration proceeds. The sample is poured through the filter being careful to decant as much of the sample as possible, before the settled precipitate clogs the filter, so as to speed up the process. The final portion with most of the precipitate is placed on the filter and allowed to filter to near dryness. As the volume is reduced the sample container is rinsed with the 2% trace metal-grade-ammonia solution and this is added on to the filter. The 2% trace metal grade ammonia solution is then used to rinse down the sides of the filter holder and the filter surface. The filter is allowed to dry and is then extracted with tweezers. The folded filter is used to wipe any precipitate that has clung to the support surface of the filtration assembly.

The filter and precipitate are put into a 50-mL pre-labeled polypropylene centrifuge tube. A calibrated repippetor is used to add 40 mL of Seastar Baseline 4% nitric-1% hydrochloric acid solution. The centrifuge tubes are tightly capped, shaken to disaggregate the precipitate into the solution and allowed to stand with periodic agitation for one to two hours so that the ferric hydroxide and co-precipitated REE's are redissolved. Low temperature and minimization of exposure time are critical to keeping the REE blanks to acceptable values. The samples are then centrifuged for one hour to separate the liquid from the quartz fibers. The liquid is decanted into a second clean polypropylene centrifuge tube and capped until analysis.

During the processing of the filtered samples, we observed that samples with high silica values (those from New Zealand) have a larger volume of precipitate upon ferric hydroxide co-precipitation

than anticipated, probably due to the formation of silica gel which hardens to translucent silica on drying. This hardened gel remains insoluble when the precipitate is redissolved. REE MDL's for the filtered samples are given in Table 1. The filtered samples that had detectable quantities of the REE's were rerun directly at a 1X dilution by ICP-MS to assess if the recovery of the REE was total or if analyte was being lost to the silica gel. The successful recovery of the lowest concentration sample implies that losses are not too severe. However, a 50% difference at 17 times the detection limit was unacceptable. We modified the procedure to eliminate drying the precipitate in an oven. This also eliminated the need to heat the samples after the acid solution had been reintroduced to encourage the ferric hydroxides to redissolve.

The method detection limits for the REE's Sc, Y, Zr, Th, and U were determined by addition of 20 mL Seastar Baseline HNO_3 to one liter of DIW in an HDPE bottle. To this was added 1 mL of a spiking solution containing Sc, Y, Zr, and REE's at 4 μg/L and Th and U at 2 μg/L. The final concentrations in the sample were therefore 4 ng/L and 2 ng/L (ppt), respectively. The spiked samples were set aside for at least one week. The iron spike is then added and the precipitation procedure is carried out on each replicate. This made the final concentration to be read at the instrument 100 ng/L and 50 ng/L (ppt), respectively. Seven replicates were spiked and prepared as well as six blanks. The blank sample bottles were carried into the field after addition of the baseline nitric acid and subsequently had deionized water added in the lab and were allowed to age for at least a week before extraction. The extracts were run at the Washington State University ICP-MS lab.
The procedure recommended in the Federal Register (40 CFR section 136) and numerous other sources, is to prepare six to ten samples for analysis following all method procedures for each sample. The Student's t for seven samples (6 degrees of freedom) at 99% confidence (3.143) is multiplied by the standard deviation of the individual determinations and the result is the method detection limit (MDL). The optimal spike amount should result in a concentration of 3 to 5 and no more than 10 times the MDL. The MDL's are summarized in Table 1. It is clear that contamination is present as minor amounts of Y, La, Ce, and perhaps U. The resulting MDL's, recalculated to original sample concentrations, range from about 8 ng/L for La and 3 ng/L for Ce to less than 2 ng/L for Pr to Lu, Th, and U. These REE MDL's are considered adequate for this project.

REE CONTENTS IN NEW ZEALAND GEOTHERMAL WATERS

The REE concentrations obtained are shown in chondrite-normalized form in a series of diagrams (Fig. 1-7). A table of all the raw data is available from the second author. The samples from geothermal areas in the Taupo Volcanic Zone, New Zealand fall into two groups. Low pH acid-sulfate water samples have been found to have elevated, light REE-enriched patterns whereas samples having near neutral pH represented by neutral-chloride and neutral-carbonate-sulfate waters have much lower REE contents and flatter patterns. Most samples are near enough to the detection limits that irregularities in the flatness of the chondrite-normalized patterns are probably caused by random variations and not by any characteristic of the samples themselves. Most of the field filtered neutral-carbonate and neutral-chloride samples have REE values near or below our method detection limits (Table 1). The corresponding unfiltered samples often had measurably higher REE concentrations. Visual estimates of suspended solids in the unfiltered samples range from undetectable to several grams per liter of sample. The contribution of REE's from suspended solids could be substantial if the total content of the solids were extracted. For example a liter of water containing 100 mg of felsic silicate having a minimal La concentration of 10 mg/kg (ppm) would contain 1000 ng/L of La if all the La could be extracted. The measured values are much lower for waters which had undetectable REE concentrations in the filtered sample.

An anomaly in Tb values for all samples, filtered and unfiltered, which had REE concentrations near the detection limits has been traced to the sample bottles which had to be purchased in New Zealand. The trip blank (NZ-U000-98) was found to have detectable REE's, Tb in particular. If the trip blank is subtracted from all the samples the Tb anomaly disappears. The sample data shown in the chondrite-normalized variation diagrams have had the trip blank subtracted. This blank contamination was not observed in method blanks made with standard HDPE bottles that had been used once already. This may however be due to subsequent use of a mixture of 2% nitric 1% hydrochloric acid for cleaning bottles.

Table 1, Method Detection Limits in Geothermal Waters

	IDL's 1X 10/20/98			MDL's for filtered samples 07/19/98				MDL's for unfiltered samples 12/16/98					
Element Isotope	1X IDL Soln [ng/L]	Spike / 1X IDL	1X IDL [ng/L]	%Spike Recovery	Spike Conc [ng/L]	Spike / MDL	Sample MDL [ng/L]	%Spike Recovery	Method Blank IDL [ng/L]	Spike Conc [ng/L]	Spike / MDL	Sample MDL [ng/L]	Sample MDL [nmole/kg]
Y 89	80	3.5	23	75%	4	0.6	6.3	174%	1.3	4	1.1	3.7	0.042
Zr 90	80	1.5	52	498%	4	0.1	30	-99%	15	4	0.7	5.7	0.063
Th 232	40	5.7	7.0	239%	2	0.7	3.0	98%	0.40	2	4.2	0.47	0.0020
U 238	40	6.3	6.3	740%	2	0.0	42	138%	0.22	2	2.3	0.87	0.0036
La 139	80	4.3	19	120%	4	0.2	21	136%	1.2	4	0.5	7.9	0.057
Ce 140	80	5.8	14	140%	4	0.8	5.0	89%	2.4	4	1.8	2.2	0.016
Pr 141	80	8.6	9.3	94%	4	3.8	1.0	85%	0.16	4	5.5	0.73	0.0052
Nd 144	80	5.1	16	99%	4	1.5	2.7	122%	0.54	4	2.5	1.6	0.011
Nd 146	80	3.0	27	100%	4	1.6	2.5	98%	0.63	4	3.5	1.1	0.0078
Sm 152 [Ba]	80	5.0	16	85%	4	3.1	1.3	85%	0.21	4	1.8	2.3	0.015
Eu 151 [Ba]	80	4.3	19	88%	4	3.2	1.3	77%	0.15	4	5.2	0.77	0.0051
Gd 157 [Pr]	80	2.1	38	86%	4	2.8	1.4	93%	1.2	4	3.2	1.2	0.0079
Gd 160 [Nd]	80	6.1	13	83%	4	3.0	1.3	109%	1.1	4	3.9	1.0	0.0065
Tb 159 [Nd]	80	11	7.4	88%	4	3.3	1.2	92%	0.05	4	5.6	0.72	0.0045
Dy 163	80	5.1	16	85%	4	2.6	1.5	89%	0.34	4	3.7	1.1	0.0066
Ho 165	80	8.5	9.4	90%	4	3.7	1.1	100%	0.10	4	6.0	0.66	0.0040
Er 168	80	3.6	22	90%	4	2.8	1.4	91%	0.22	4	3.4	1.2	0.0071
Tm 169	80	8.8	9.1	90%	4	3.6	1.1	89%	0.05	4	4.8	0.83	0.0049
Yb 174	80	5.7	14	100%	4	1.8	2.2	87%	0.27	4	3.3	1.2	0.0071
Lu 175	80	9.3	8.6	90%	4	3.2	1.3	84%	0.06	4	5.7	0.70	0.0040

REE's are corrected for oxide interference by elements in [brackets]
Unrounded results have at most 2 significant figures
MDL's of 7/19/98 used 47 mm quartz fiber filters and reduced 1 liter to 20 mL
1X IDL's of 10/20/98 from multiple analyses of an IDL solution
IDL's of 12/16/98 unspiked blank samples with no Si addition, used 90 mm quartz fiber filters, and concentrated 1 liter to 40 mL
MDL's of 12/16/98, 300 mg Si equivalent to 600 mg/L silica added with spike, used 90 mm quartz fiber filters, and concentrated 1 liter to 40 mL

There is a correlation of increasing total REE's with decreasing pH (not shown) (c.f. Lewis et. al., 1997; geothermal waters at Yellowstone) and also with increasing sulfate (not shown). We found that application of our silica values to the quartz geothermometer (Fournier et al, 1981) with no steam loss gave essentially the same maximum temperature values as those obtained by Mongillo and McClelland (1984). There is a positive correlation of total REE's with silica (not shown) for the acid-sulfate waters. However, in those fields for which we have neutral-chloride samples, silica concentrations of the acid-sulfate waters do not reach the highest values characterized by the higher temperature neutral-chloride reservoirs. These observations suggest that the highest REE values are typically generated by acid-sulfate waters under slightly cooler conditions than that of the main source of chloride waters.

The samples from the Te Kopia, Rotokawa, Mount Ruapehu, and Waiotapu all have low-pH acid-sulfate waters. Both Waiotapu and Rotokawa have deep neutral-chloride waters and those of Rotokawa can be shown to form mixing lines with the acid-sulfate waters (personal communication, Bruce Christenson, 1998). These low-pH acid-sulfate waters have light REE-enriched patterns with a small negative Eu anomaly as might be expected from waters which have interacted with felsic silicates (Figures 1, 2, 3). The acid-sulfate samples were unusual in that the filtered samples from Te Kopia, Rotokawa, and Waiotapu contained higher REE concentrations than the corresponding unfiltered samples. The acid-sulfate waters from Frying Pan Lake at Waimangu (NZ-011-98) have a pH of about 5.7 and very low REE values but higher than those of the neutral and higher pH samples. The Waimangu samples may have a light REE-enriched chondrite-normalized pattern but it is difficult to determine as the heavy REE concentrations (although plotted) are generally below our method detection limits (Figure 4).

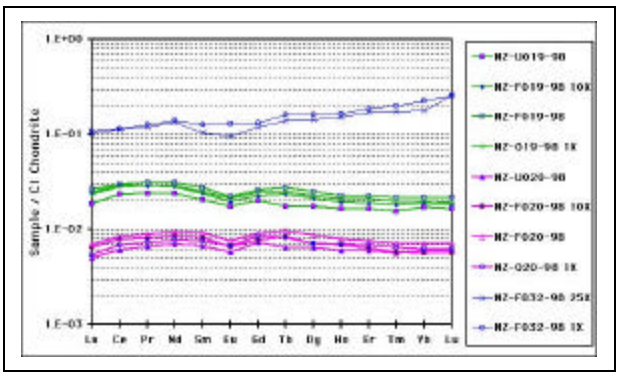

Fig. 1. C1-Chondrite normalized REE concentrations from Mt Ruapehu NZ-032-98; and Rotokawa NZ-019-98 and NZ-020-98

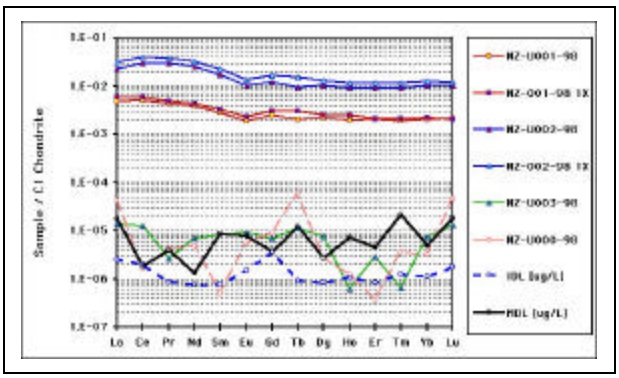

Fig.3. C1-Chondrite normalized REE concentrations from Waiotapu: NZ-001-98, NZ-002-98, NZ-003-98 also shown: MDL, IDL and NZ-000-98

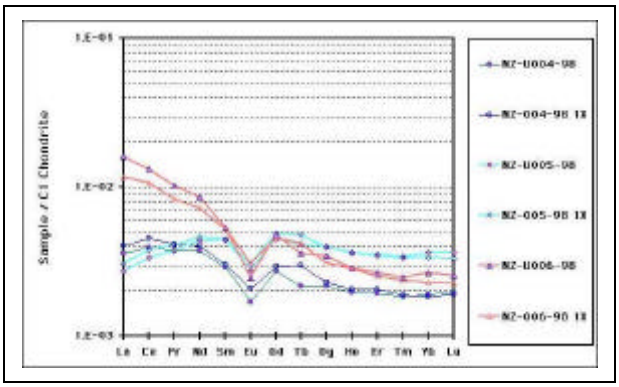

Fig. 2. C1-Chondrite normalized REE concentrations from Te Kopia Reserve: NZ-004-98, NZ-005-98 and NZ-006-98

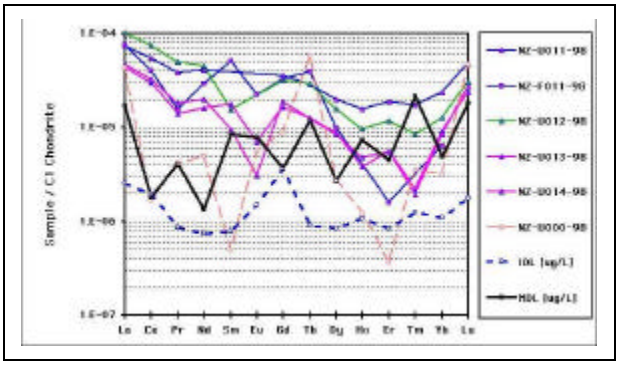

Fig.4. C1-Chondrite normalized REE concentrations from Waimangu NZ-011-98 through NZ-014-98; also shown MDL, IDL and NZ-000-98

The Waiotapu thermal reserve samples (NZ-001-98 to NZ-003-98) present the most striking contrast in REE contents (Figure 3). Champagne Pool which is the definitive chloride feature of the Waiotapu reserve, has REE contents at least (limited by our MDL's) three orders of magnitude lower than those of the acid-sulfate samples. Note the Tb contamination of the trip blank (NZ-000-98). The REE patterns of the Waiotapu acid-sulfate waters were similar those of the Rotokawa and Te Kopia thermal reserves (Figures 1, 2). Waiotapu has stored heat equivalent to that of the Wairakei and Broadlands fields. It would seem that deep chloride waters with the highest flow rates have the lowest total REE concentrations.

The samples from the Wairakei and Broadlands fields are near or below detection for the REE's. However, the high pressure samples taken with the Weber sampler seem to have slightly higher values than samples that flashed at atmospheric pressure (Figure 5). This suggests that rapid boiling may cause the loss of the REE's, possibly to scale, thus hiding the true signature of the geothermal fluids. The De Bretts sample (Figure 5, NZ-031-98) is a moderately flowing hot spring of low-conductivity near neutral-pH water within the Tauhara-Taupo Field which has both acid-sulfate and neutral-chloride waters. These waters all have negatively sloped light REE-depleted chondrite-normalized patterns. The De Bretts thermal park is near the Wairakei area and the similarity in their REE patterns is suggestive that they share either a common source of ground water or similar stratigraphic sections.

The Te Aroha samples are near neutral pH, high carbonate fluids. The Te Aroha cold spring (NZ-009-98) and hand pumped thermal well (NZ-010-98) both contained measurable amounts of REE's (Figure 6).

In contrast, REE's in the Te Aroha geyser (NZ-008-98) were below detection. The Orakeikorako samples were very low in REE's (NZ-016-98) but the diamond geyser (NZ-017-98, not shown) had the lowest REE values of that field. Samples with measurable REE concentrations from Orakeikorako and Te Aroha have little or no slope in the chondrite-normalized plots (Figure 6).

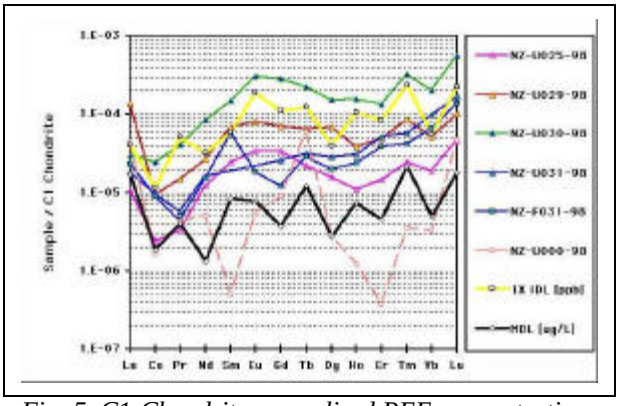

Fig. 5. C1-Chondrite normalized REE concentrations from Wairakei NZ-025-98, Broadlands NZ-029-98, NZ-030-98 De Bretts NZ-031-98, NZ-000-98 and MDL.

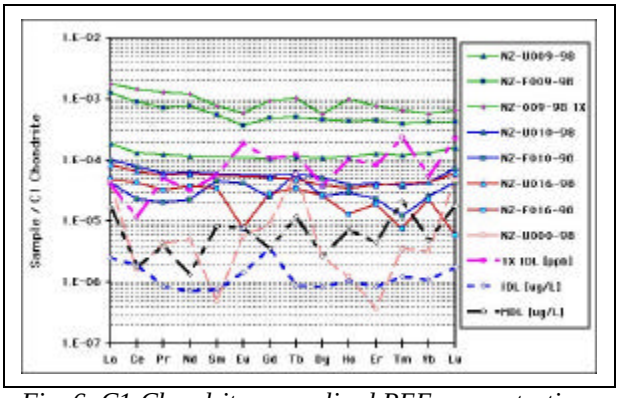

Fig. 6. C1-Chondrite normalized REE concentrations from Te Aroha NZ-009-98, NZ-010-98, Orakeikorako NZ-016-98, 1X IDL and MDL

The samples from Morere and Te Puia (Figure 7, NZ-021-98 through NZ-024-98) are thought to be associated with dewatering from the subduction zone in Eastern New Zealand. These samples have low REE contents which are similar in concentration to those of the Wairakei and Broadlands mixed chloride waters (Figure 5). The Morere and Te Puia samples have a positive anomaly for Eu and Sm (Figure 7) which is caused by the difficulty of correcting these two elements for isobaric interference from barium oxides. These samples were unusually high in barium.

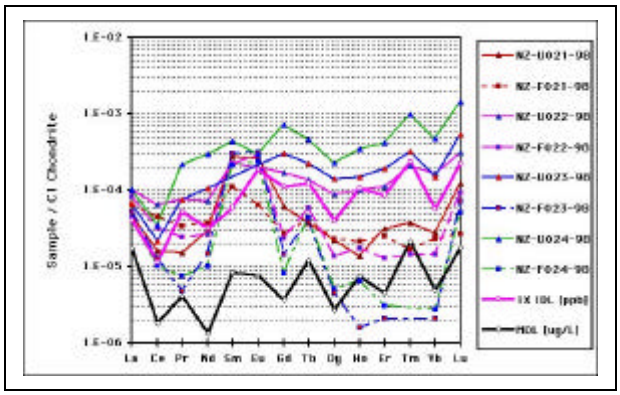

Fig. 7. C1-Chondrite normalized REE concentrations from Morere NZ-021-98, NZ-022-98, Te Puia NZ-023-98, NZ-024-98, and MDL.

SUMMARY AND CONCLUSIONS

Low-pH geothermal fluids may have higher REE concentrations for three reasons: 1) low pH supports greater solubility of the REE's in solution; 2) low-pH waters are much more effective in dissolving the country rock and leaching the REE's 3) Low-pH waters generally have lower flow rates and therefore, lower water-to-rock ratios. The De Bretts hot spring, and Te Aroha cold spring, although near neutral in pH, may have higher REE's because the water-to-rock ratio is lower. Another possibility is that the higher sulfate content of the Te Aroha fluids might indicate that an acid-sulfate fluid has been neutralized but still retains a more elevated REE signature.

For neutral-chloride and neutral-carbonate-sulfate waters having very low or undetectable REE concentrations, the unfiltered samples usually have higher REE values. Even a few milligrams of Felsic silicate material could introduce higher values than those observed if completely extracted. We conclude that the REE concentrations observed represent leachable values from surface adsorbtion of REE's on the suspended solids. In contrast to this, surface adsorption after sampling may be responsible for slightly lower REE concentrations in the unfiltered samples of acid-sulfate waters, which usually had slightly higher REE concentrations in the unfiltered samples.

The samples from the Wairakei and Broadlands fields as well as Te Aroha and Orakeikorako all have at least one example where geyser activity or flashing at atmospheric pressure may be responsible for loss of

the REE's, possibly to scale, possibly to surface adsorption on suspended solids, hiding the magnitude but possibly not the pattern of the true signature of the deeper geothermal fluids. The Wairakei and Broadlands waters have measurable REE concentrations only in the unfiltered samples. However, these samples may still represent a significant fingerprint of the total REE concentrations in the deep geothermal fluids if surface adsorption and desorption are the dominant sink and source, respectively, of the REE concentrations in these unfiltered samples.

The concentrations of REE's in the geothermal fluids of the Taupo Volcanic Zone can easily span 4 orders of magnitude. By analysis of both filtered and unfiltered samples, we have demonstrated that surface adsorption effects are significant at the very low concentrations of REE's which can occur in geothermal fluids. Although lower detection limits may be achievable with better instrumentation we suggest that surface adsorption, and scale formation may be a significant mechanism masking the true signature of the deepest fluids. We plan to test the possible loss of REE to scale by analyzing scale samples for TVZ geothermal fields for REE content.

Fields with a high flow rate and high geothermal potential may have lower REE concentrations because they have moved larger volumes of groundwater through their plumbing systems. This may have effectively leached the easily available REE's. However, this explanation seems unlikely given the measurable REE concentrations that can result if a significant fraction of the total REE's in the wall rock or suspended solids were to be assimilated. A related possibility is that high water-to-rock ratios in a through-flowing system dilute the REE that do dissolve. The water-to-rock ratio is important both in terms of dilution effects and the time water spends in contact with the rock. Therefore, it may be that the REE contents of geothermal fields with high fluid and heat production may be expected to reflect only the REE content of the cooler meteoric water which is flowing into the system. This hypothesis would need to be tested by analyzing meteoric waters sampled from the recharge areas of geothermal fields and comparing the REE contents to those of the discharged waters.

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