

EXPERIMENTAL STUDY ON RARE EARTH ELEMENT MOBILITY DURING GREYWACKE - WATER INTERACTIONS

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Keywords: REE, flow-through experiments, water-rock interactions, greywacke.

ABSTRACT

Due to the increase demand in Rare Earth Elements necessary in solar panels or wind turbine magnets, the source and mobility of REE in geothermal fluids is becoming increasingly interesting. Previous studies of geothermal fluids from Taupo Volcanic Zone (TVZ) indicate that some REE are released during the breakdown of primary phases due to hydrothermal alteration. However, there is limited experimental data on the processes controlling the behaviour of REE in geothermal systems of Aotearoa New Zealand. The results presented here comprise part of a larger project that aims to broaden the understanding of the chemical exchange between geothermal fluids and reservoir rocks occurring during recharge of the geothermal plume.

In this preliminary study, we have investigated experimentally the release of REE during fluid-rock interaction using a continuous flow apparatus under hydrothermal conditions. The experiment used a “unaltered” greywacke as a proxy for the dominant basement rock in the Taupo Volcanic Zone. Distilled water was used as the fluid. The greywacke was progressively heated from ambient temperature to 400°C in 50°C increments over a period of 126 days. The fluid flow rate was 1 ml hr⁻¹ for the entire experiment.

Results indicate that measurable concentrations of REE are released to the fluid from the greywacke. The similarity of REE patterns to other species present in the solution (i.e. Fe, H₂S, SO₄²⁻) suggests that their trends are controlled mainly by mineralogy. However, the concentration of REE is strictly dependent on temperature and pH. These results show that the basement greywacke in the TVZ does influence the REE composition of the geothermal fluid. The research findings are discussed and compared with available historical data.

1. INTRODUCTION

The knowledge of the mobility of the rare earth elements (REE) in geothermal fluids is important, as REE are useful indicators of various geochemical processes (e.g., Hopf, 1993, Wood, 2003, Hannigan, 2005). The REE composition of hydrothermal fluids is influenced by the solubility of REE-bearing minerals and the stability of REE complexes in aqueous solutions at elevated temperature and pressure (Wood, 2003). In the past 20 years, progress in understanding the behaviour of REE under hydrothermal geothermal conditions has been made, principally to the development and continuous enhancement of inductively coupled plasma-mass spectrometry (ICP-MS). This has allowed rapid and accurate analysis of REE at ppt levels. Nevertheless, there is still lack of data on the solubility of REE-bearing minerals, the partitioning of REE between rock-forming minerals and hydrothermal solutions, and their behaviour during water-rock interactions at geothermal temperatures (200 – 400°C).

To date, there have been several experimental studies conducted on the REE behaviour under hydrothermal conditions which demonstrate that the REE are mobile to some degree. For example, Menzies et al. (1979) tested REE mobility during greenstone-sea water interactions up to 350°C. Terakado et al. (1993) investigated the behaviour of REE during rhyolite-water interactions at 250°C. Kikawada et al. (2001) experimentally studied mobility of REE during andesite – water interaction experiments. Douglas and Seyfried (2005) studied mobility of REE between peridotite and aqueous fluid at 400°C. Limited experimental and theoretical work, however, has been performed to constrain the role of fluid and rock composition on the overall distribution of REE in fluids in geothermal systems, especially for the chemical and physical conditions applicable to hydrothermal systems in the Taupo Volcanic Zone (TVZ).

The TVZ is a rifting arc resulting from the westward subduction of the Pacific Plate underneath the Australian Plate (Figure 1). It is divided into three segments based on the composition of the eruptive products. The southern part, the Tongariro National Park, and the northern part from Kawerau to White Island, are dominated by andesitic arc magmatism, while the central TVZ has been dominated by large volume of rhyolitic magmatism with rare basalt and andesite with a greywacke metasedimentary basement (Reid, 198; Hopf, 1993; Chambefort, 2021). TVZ geothermal fluids are dominantly meteoric water. The composition of the fluid circulating in the geothermal system is determined by the dissolution and precipitation of minerals in the aquifer rocks with various amount of magmatic volatiles (e.g., CO₂). The entrainment of surface waters, which also contain measurable concentrations of REE (Wood, 2003; Hannigan, 2005), provides an initial input to the geothermal REE profile. However, regarding the modification of these profiles after groundwater circulation, there has been no experimental study of the relative influence of the TVZ basement rocks on REE patterns.

The preliminary work on the REE presented here represents part of the results from fluid-rock interaction experiments being currently undertaken in the Experimental Geochemistry Laboratory at GNS. The broader study aims to understand the influence of the TVZ basement greywacke on fluid chemistry in the deep portions of geothermal systems.

2. METHOD

2.1 Apparatus

The flow-through autoclave (Fig. 1) reproduces high temperatures and pressures (ambient to 400°C, atmospheric to 500 bars) and enables continuous fluid flow between 0.001 to 15 ml min⁻¹. Fluid flow is maintained by a computer-controlled double-piston metering pump. The pump delivers distilled water into the bottom of a titanium separator containing a movable piston. The experimental fluid, contained above the piston, is pressurised and forced through the system. The fluid flows through titanium tubing and into the titanium pressure vessel (internal diameter 25 mm x 150 mm length, 19.3 ml internal volume) containing the rock substrate. The pressure vessel is externally heated in an oven. Experimental parameters are continuously recorded digitally.

The flow-through apparatus temperature is monitored by a thermocouple inserted into the top of the pressure vessel and pressure is maintained by a back-pressure regulator (BPR) connected with the top of the pressure vessel. All wetted parts of the flow-through apparatus in contact with the experimental fluid are composed of titanium except for the Teflon diaphragm in the BPR. Samples are collected daily in a syringe connected to the BPR.

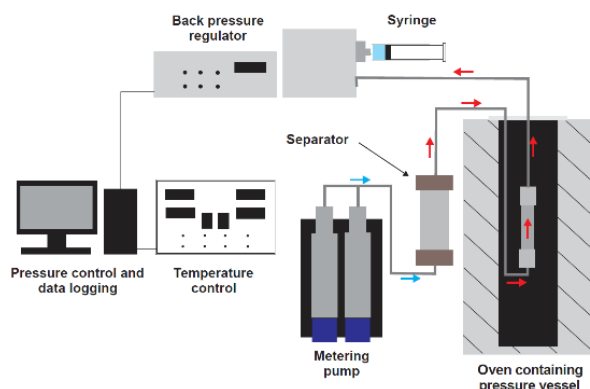


Figure 1: Schematic diagram of the high temperature and pressure hydrothermal flow simulator.

2.2 Rock Substrate

The rock used was a greywacke sourced from the Wautu Quarry, west of Tokoroa, New Zealand. The rock was crushed and sieved to retain the 0.35 – 0.5 mm size fraction which was cleaned ultrasonically to remove fine material.

2.3 Experimental Fluid

The fluid used was doubly distilled water (18.2 MΩ cm⁻¹) and deoxygenated with a N₂:H₂ gas mixture. The pressure and temperature conditions for the experiments are shown in Figure 2.

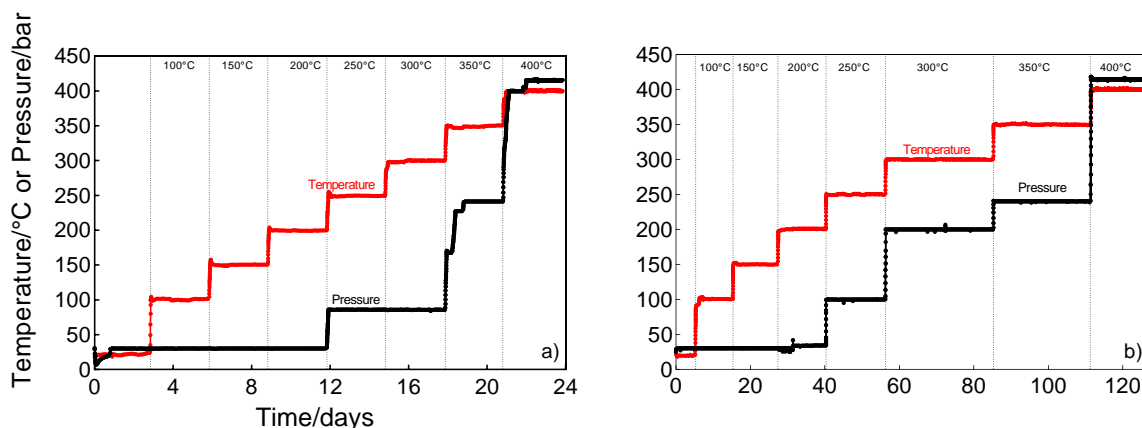


Figure 2: Pressure-temperature path for a) the control experiment with empty pressure vessel and b) for the Wautu greywacke.

2.4 Analyses

An effluent sample was collected every 24 hours for analysis of pH, major cations (Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B, and SiO₂) by ICP-OES, anions (Cl⁻ and SO₄²⁻) by IC. H₂S was determined by methylene blue method/UV-Vis spectroscopy. The REE contents were determined by inductively coupled plasma-mass spectrometry (ICP-MS). A ThermoFisher iCAPQ ICP-MS was employed. Oxide formation, as measured by ¹⁵⁶[CeO]/¹⁴⁰Ce, was typically less than 0.5%. Mathematical corrections for isobaric oxide interferences were applied for BaO on Eu and Sm, PrO on Gd, and NdO on Tb (Chien et al. 2006). Indium and Rhenium were employed as internal standards. For more details on the analytical protocol for the REE see Shannon et al. (2005).

3. RESULTS AND DISCUSSION

3.1 Chemical composition, and pH of reacted fluids

The experimental temperature has a strong influence on reacted fluid composition during the greywacke-water interaction experiment. The trends are consistent with previous experimental data (Mountain et al. 2016). Each increase of experimental temperature results in an increase of concentrations of REE (Figure 3) up to 350°C. During the control experiment the concentrations of major elements and REE were below detection limits at each temperatures and are not shown.

After the increase to 200°C, 300°C, and 350°C, there are transient increases in REE concentration. Among the major elements similar trends are present for Fe, SO_4^{2-} and H_2S . This suggests that mobilisation of the lanthanides occurs by a similar mechanism to these species. Temperature increases are also accompanied by a shift in pH. The measured $\text{pH}_{25^\circ\text{C}}$ decreases by several units, after each temperature change, and then gradually increases to a new stable level. The decreases in pH coincide with the highest REE concentrations (Figure 3b). As pH increases, REE concentrations decrease. In general, after each temperature increase, the REE-bearing minerals dissolution kinetics are faster than the processes that buffer pH. It has been previously reported that in some environments the major REE mobilisation controlling factors are high sulphate concentration and low pH (Wood, 2003; Abreu and Morais, 2010; Sapsford et al. 2012). It is therefore, conjectured that REE are mobilised after temperature change due to pH decrease and SO_4^{2-} concentration after which they precipitate, eventually as $\text{M}_2(\text{SO}_4)_3$ (Kim and Osseo-Asare, 2012). Another possible mechanism is REE scavenging by Fe (III) oxyhydroxide precipitates generated by fluid-rock interaction (Sapsford et al. 2012; Beermann et al. 2017). In summary, higher REE concentrations at lower pH are explained by faster mineral dissolution rates at lower pH. Further experiments could targeting specific minerals in order to refine the origin of the REE.

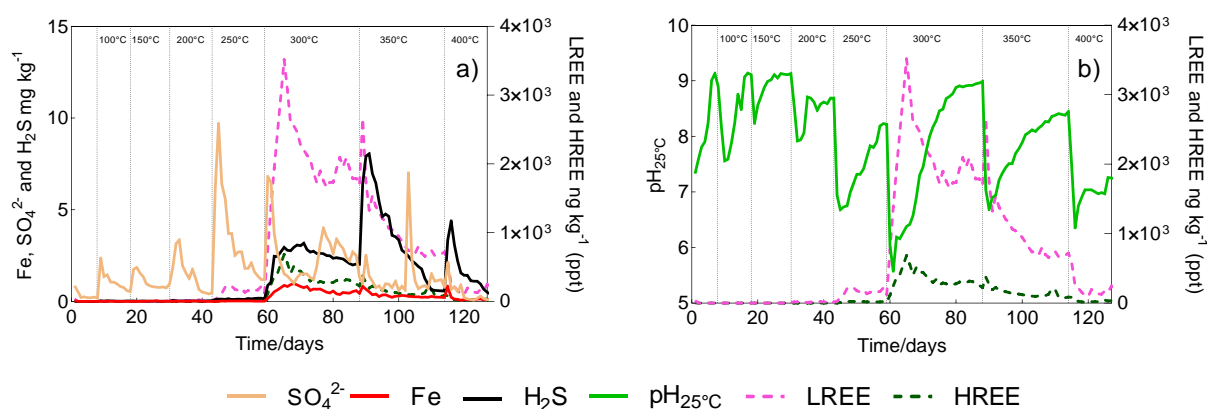


Figure 3: LREE, HREE, Fe, H_2S , SO_4^{2-} concentrations a) and pH b) in effluent samples from the water-greywacke interaction experiment.

3.2 Correlation matrix

In order to investigate the relationship between the REE and other dissolved species, correlation coefficients have been calculated (Table 1). The correlation analysis was performed using Spearman correlation coefficients (GraphPad) on the raw data from the ICP-OES and ICP-MS. The Spearman technique is preferable, over Pearson correlation calculations, since it is nonlinear, nonparametric, and robust, therefore reducing the effect of outliers which are very likely to be present in geochemical datasets (Garrett et al., 2017; de Campos and Licht, 2021). A separate calculation was completed for each temperature except 22, 100 and 150°C., as REE concentrations were close to or below detection limits at these temperatures.

The results show complexity of the greywacke-water interaction. At all temperatures, the HREE and LREE behave similarly. At 200 °C dissolution of lithium-bearing silicate minerals, such as chlorite or plagioclase are likely to be responsible for increased REE concentration. At 250°C dissolution of magnesium-rich minerals may explain REE release. At 300 and 350 °C, correlation of REE with multiple dissolved species, suggests that more than one mineral phase is contributing to REE release. At these temperatures, REE behave most similar to Fe and H_2S , suggesting that they may originate from the dissolution of pyrite. At 400 °C, REE decrease in concentration and is comparable to Ca and K behaviour, which suggests that the REE are being trapped in a secondary K-bearing secondary phase(s).

3.3 REE patterns

REE concentrations in the unreacted greywacke are several orders of magnitudes higher than in the fluid (Table 2). The highest REE concentrations in the fluid samples was measured after 5 days at 300°C. Note that REE concentrations of all fluid samples are significantly greater than the starting fluid or the control experiment samples. Figure 4 shows cumulative concentration of REE at each of the temperatures normalised to chondrite (Figure 4a) and to Waotu greywacke (Figure 4b). The results from this study are compared to Waiotapu results, as the fluid chemistry from this area is likely to be influenced by underlying greywacke basement (Hedenquist, 1991).

Table 1. Spearman correlation coefficients calculated for two variables for the 200 - 400°C data sets. Green boxes highlight significant correlations using a confidence level of 95% ($\alpha = 0.05$).

temperature	v	r		Ca	Fe	K	Li	Mg	Mn	Al	Na	Mo	Cl ⁻	SO ⁴	H ₂ S	SiO ₂	As	LREE
200°C	11	0.553	LREE	0.478	0.204	0.492	0.570	-0.601	0.000	-0.138	-0.302	0.000	-0.204	-0.322	0.007	0.656	-0.603	1.000
			HREE	0.423	0.052	0.088	0.289	-0.649	0.000	0.190	-0.154	0.000	-0.186	-0.058	0.178	0.268	-0.496	0.775
250°C	14	0.497	LREE	-0.112	0.195	0.194	-0.202	0.612	-0.420	-0.132	-0.544	-0.146	-0.162	0.150	0.114	0.349	0.091	1.000
			HREE	-0.174	0.244	0.271	-0.236	0.649	-0.420	-0.085	-0.579	-0.180	-0.174	0.168	0.087	0.355	0.041	0.953
300°C	25	0.381	LREE	0.304	0.713	0.313	0.302	0.586	0.606	-0.139	-0.278	-0.377	0.355	-0.586	0.656	-0.044	0.164	1.000
			HREE	0.389	0.655	0.410	0.430	0.600	0.593	-0.244	-0.348	-0.461	0.494	-0.532	0.749	-0.084	0.293	0.916
350°C	23	0.396	LREE	0.751	0.923	0.826	-0.848	0.781	0.937	-0.642	-0.140	-0.512	-0.403	-0.012	0.930	-0.651	0.000	1.000
			HREE	0.492	0.724	0.787	-0.754	0.521	0.748	-0.445	-0.236	-0.215	-0.390	0.013	0.716	-0.445	0.000	0.732
400°C	12	0.532	LREE	0.592	0.402	0.785	0.444	0.471	0.199	0.253	0.645	0.182	0.396	0.090	0.128	-0.256	0.111	1.000
			HREE	0.066	0.424	0.508	0.124	0.385	0.338	0.477	0.401	0.065	0.294	0.002	-0.273	-0.590	-0.318	0.736

LREE: La, Ce, Pr, Nd, Sm, Eu, Gd; HREE: Tb, Dy, Ho, Er, Tm, Yb, Lu; v – degrees of freedom (v = number of samples – 2); r – the critical value of the correlation coefficient at 5 percent level of significance

Chondrite-normalised results show that the REE patterns of the experimental solutions parallel with the whole rock REE pattern, which is characterised by a small LREE enrichment. During the lower temperature stages of the experiment (i.e. 200 °C), a positive Eu anomaly is present and is attributed to dissolution of Eu-bearing phases (e.g., plagioclase). The chondrite-normalised patterns for neutral chloride waters from Waiotapu have a similar pattern showing a similar positive Eu anomaly. The two comparable patterns could reflect the influence of greywacke basement rock at similar temperatures (i.e. ~200 °C) on the Waiotapu neutral chloride water composition.

At 250°C and greater, a similar LREE enrichment is visible (Fig. 4a). Note that at these temperatures, Eu shows a negative anomaly suggesting less efficient dissolution or more effective re-precipitation of Eu within compatible minerals. Negative Eu anomaly has been previously reported by Shibata et al. (2006) and explained by Eu²⁺ compatibility with the crystal structure of plagioclase in comparison to other REE. A similar Eu anomaly is observed in Waiotapu acid-sulfate waters, also suggesting a greywacke influence on Waiotapu fluids.

In comparison, when the experimental results are greywacke-normalised, a modest enrichment of the HREE in the fluid is observed (Figure 4b). Waiotapu neutral chloride waters mirror the pattern of the 200°C results. Waiotapu acid-sulfate waters in contrast are unlike the higher temperature results. The relatively flat REE pattern, when normalised to the rock, implies that the REE are not significantly fractionated by water-rock interaction.

Table 2. REE concentration (mg kg⁻¹) in the unreacted rock and during fluid-rock interaction at 300°C.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Waiotapu greywacke	18.60	38.50	4.79	19.60	4.71	1.16	4.00	0.60	3.90	0.78	2.19	0.32	2.50	0.33
Fluid at 300°C after 5 days	6.27 x 10 ⁻⁴	1.48 x 10 ⁻³	1.99 x 10 ⁻⁴	6.88 x 10 ⁻⁴	2.13 x 10 ⁻⁴	4.82 x 10 ⁻⁵	2.59 x 10 ⁻⁴	4.02 x 10 ⁻⁵	2.65 x 10 ⁻⁴	5.02 x 10 ⁻⁵	1.47 x 10 ⁻⁴	2.11 x 10 ⁻⁵	1.43 x 10 ⁻⁴	1.93 x 10 ⁻⁵
Waiotapu neutral chloride waters (i)	4.50 x 10 ⁻⁶	7.70 x 10 ⁻⁶	7.20 x 10 ⁻⁷	3.20 x 10 ⁻⁶	5.30 x 10 ⁻⁷	1.30 x 10 ⁻⁶	6.50 x 10 ⁻⁷	9.10 x 10 ⁻⁸	5.30 x 10 ⁻⁷	1.20 x 10 ⁻⁷	3.20 x 10 ⁻⁷	5.70 x 10 ⁻⁸	3.90 x 10 ⁻⁷	6.30 x 10 ⁻⁸
Waiotapu acid-sulfate waters (i)	2.60 x 10 ⁻³	6.60 x 10 ⁻³	8.20 x 10 ⁻⁴	3.20 x 10 ⁻³	8.10 x 10 ⁻⁴	2.00 x 10 ⁻⁴	8.70 x 10 ⁻⁴	1.40 x 10 ⁻⁴	8.60 x 10 ⁻⁴	1.70 x 10 ⁻⁴	5.00 x 10 ⁻⁴	7.20 x 10 ⁻⁵	4.60 x 10 ⁻⁴	7.00 x 10 ⁻⁵

(i) Wood, 2003

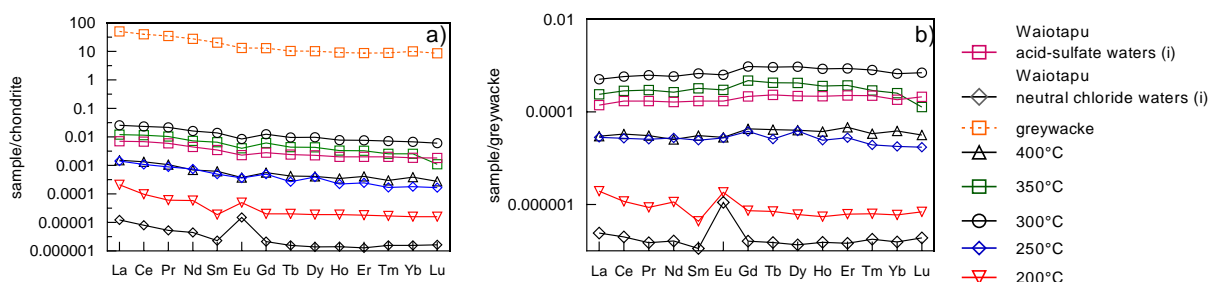


Figure 4: a) Chondrite-normalised and b) Waiotapu greywacke-normalised REE patterns for Waiotapu waters (Wood, 2003), Waiotapu unaltered greywacke and the experimental solutions. Chondrite values from Taylor and McLennan (1985).

3. CONCLUSION

Here we present a reconnaissance study on REE mobilisation during a flow-through experiment between distilled water and greywacke. A similar control experiment without rock shows that the apparatus does not affect the REE concentrations. The greywacke-water experiment revealed:

- (1) relatively little fractionation between REE occurred between distilled water and greywacke;
- (2) a decrease in pH coincides with REE concentration increase;
- (3) the fluid REE pattern reflects the REE pattern of the greywacke and is characterised by modest LREE enrichment (when normalised to chondrite);
- (4) REE pattern normalised to the chondrite ? at 200°C show positive Eu anomaly;
- (5) at $\geq 250^{\circ}\text{C}$ REE pattern show a negative Eu anomaly;
- (6) the highest REE mobilisation rate is exhibited at 350°C and decreases at 400°C;
- (7) correlation analysis suggests that REE are leached into solution from more than one mineral phase at higher temperature;
- (8) the measured fluid REE patterns are similar to those of Waiotapu neutral chloride water, suggesting a control by greywacke.

4. ACKNOWLEDGEMENTS

Funding from GNS Science C05X1702: Strategic Science Investment Fund, New Zealand's Geothermal Future is acknowledged.

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