REE in Continental Geothermal Systems of New Zealand

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We have collected data on rare earth element (REE) contents in fluids from geothermal systems in New Zealand, including those within and outside of the Taupo Volcanic Zone on the North Island, and on the South Island. In general, pH is the dominant control on REE concentration. Low-pH, acid-sulfate geothermal fluids have relatively high REE contents (10^0 to 10^{-3} chondrite) with characteristic "gull's-wing" chondrite-normalized patterns. Except for La, Ce and Pr, which are depleted, the chondrite-normalized patterns are subparallel to those of potential host rocks, i.e., with a generally negative slope. REE concentrations in filtered and unfiltered aliquots of low-pH thermal waters are nearly equal, suggesting that most REE are present as dissolved species. Near-neutral to alkaline chloride-bicarbonate geothermal fluids have lower REE concentrations ($<10^{-6}$ to 10^{-3} times chondrite). Such fluids most commonly display LREE-enriched chondrite-normalized patterns, with variable Eu anomalies, and these are generally sub-parallel to patterns for potential reservoir rocks. The main exceptions are fluids from Taupo-Tauhara, which exhibit strong HREE-enrichment. Filtered aliquots of chloride/bicarbonate thermal waters typically contain substantially less REE than the unfiltered aliquots, suggesting that much of the REE are present in particulate form. Temperature plays a secondary role in controlling REE systematics, but may play a role in determining the nature of Eu anomaly. Fluids with higher inferred deep reservoir temperatures often, but not invariably, have strong positive Eu anomalies. There do not appear to be any major differences in REE systematics between fluids from within and outside of the TVZ (with the possible exceptions of Morere and Te Puia). In a number of cases, thermal waters were sampled two or three different times over the course of several years. In some cases, e.g., the Champagne Pool at Waiotapu, there does not seem to be very much variation in absolute REE content or in the chondrite-normalized patterns over this time period. In other cases, e.g., the Mount Ruapehu crater lake, substantial changes have occurred over the space of several years. The changes in the chemistry of the Ruapehu crater lake appear to be connected with observed eruptive activity in 1995-1996. Finally, there is some evidence that vapor phase separation, with its concomitant loss of acid volatiles and increase in pH, results in the loss of REE via precipitation/sorption. However, additional studies are required to clarify the extent of this process.

Geological applications of the HelEx 193nm laser ablation system coupled to a Nu Plasma -ICPMS

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We report the initial results of a research program coupling a HelEx 193nm excimer laser ablation system to the Nu Plasma MC-ICPMS. HelEx ('Helium Excimer') is an ablation system designed and built by Laurin Technic and the Australian National University around a Lamdba Physik Compex 110 ArF laser. The system employs an objective lens to project and demagnify a laser-illuminated aperture onto the sample; a wide range of aperture sizes, combined with different demagnification settings allows for a variety of power density/spot size combinations. The aperture-imaging optics produce uniform energy density profiles across the ablation site, while ablation in helium maximises sample transmission to the ICP (e.g., Eggins et al., 1998). The new system allows analysis of materials up to 100mm square, with rapid signal response, and also enables ablation along complex pre-defined paths.

The Nu Plasma MC-ICPMS is a double focussing mass spectrometer equipped with 12 Faraday cups and three ion counters in a novel fixed collector configuration. Steering of the ion beams into the collector array is achieved by means of a zoom lens which alters the dispersion of the mass spectrometer. The system used in the present study is equipped with the new large interface pump (Big-80) providing enhanced sensitivity.

Many of the features of both systems are ideally suited to laser ablation analysis of geological materials. Preliminary tests reveal sensitivities considerably better than those reported in the current literature. In addition the versatility of the HelEx system has proved invaluable in many situations. Ablation of high aspect ratio rectangular pits rather than spots allows for efficient sampling of material showing fine-scale sub-parallel compositional zonation e.g. speleothems. However, ablation may also be performed dynamically using small spot sizes and higher repetition rates tracking closely along complex paths e.g. mineral growth zones. The zoom optics of the Nu Plasma allow for rapid change in mass dispersion during ablation, an essential prerequisite to performing complex jumping routines during the relatively short periods of time available for analysis with laser ablation. Examples demonstrating these capabilities will be presented.

References

Eggins, S.M., Kinsley, L.K. and Shelley, J.M.G. (1998), *Applied Surface Science* **127-129**, 278-286.