

Variations of the rare earth element abundances in hydrothermal waters from the Yellowstone hydrothermal system, Wyoming, USA.

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Introduction

The Yellowstone hydrothermal system is situated in a continental extensional setting. Locally-derived meteoric water has undergone extensive interaction with both igneous and sedimentary rocks in the Yellowstone region at temperatures up to 300°C. The waters emerge over a range of temperatures up to boiling point (93°C) and have a variable chemistry, related to the type of rock with which the waters have been in contact and the processes in which they have been involved (Fournier, 1989). Hydrothermal areas are distributed around major faults (Fig. 1). Information on the transportation of metals in an aqueous environment has environmental applications. The *REE* are produced in significant amounts during fission of U and Pu (present in high-level wastes

from nuclear reactors): also they may be used as a chemical analogue for the behaviour of some of the trivalent actinides (Wood, 1990). Fluid *REE* chondrite-normalised patterns reflect the mineralogy of the rock with which it has interacted, the mineral phases which are being altered, fractionation processes and the hydrothermal fluid chemistry. The *REE* rock-normalised pattern of resulting sediments, deposits or mineral phases can elucidate further the history of the hydrothermal system. Important complexes proposed for *REE* mobilisation include chloride (Cl^-), sulphate (SO_4^{2-}), fluoride (F^-), hydroxide (OH^-) and carbonate (CO_3^{2-}) ligands.

Results

There are high concentrations of *REE* (50–150 ppb) in most of the low pH waters and the *REE* are readily detectable in all of the hydrothermal waters with $\text{pH} \leq 3.5$. Although the lowest pH waters are not confined to any particular geyser basin, they are restricted to topographically higher ground. The lowest pH of 2 was recorded at Monument Geyser Basin (MGB) and Sylvan Springs in the Gibbon Geyser Basin area, these also had the highest reported concentrations together with Horseshoe and Echinus, from Norris Geyser Basin (NGB) and Lone Star 2 from Upper Geyser Basin (UGB). Low pH waters with low *REE* content were recorded from Clearwater Springs and Crater Hills (and the meteoric waters). *REE* abundances varied between the two sampling seasons (autumn, 1991 and spring 1993).

Discussion

Total *REE* abundance is broadly inversely proportional to pH. Thermodynamic modelling predicts that fluoride complexes are the most likely candidates for *REE* transport in this type of hydrothermal solution. However, below pH 3.5 the H^+ ion competes with the *REE* for the

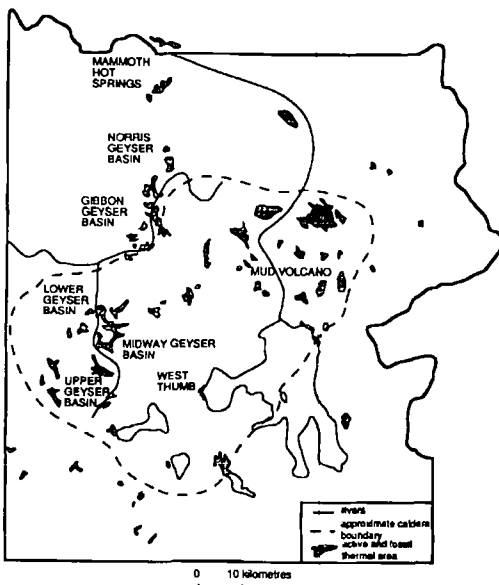


Fig. 1. Map of Yellowstone National Park showing main hydrothermal areas.

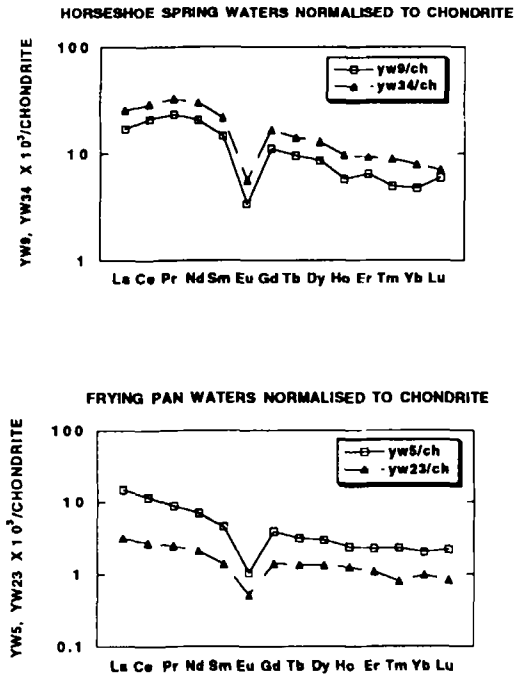


FIG. 2. Variations in *REE* abundances related to seasonal changes. Open squares are autumn 1991 data, filled-in triangles are spring 1993 data.

fluoride ion. Sulphate, produced by oxidation of hydrogen sulphide boiling off from alkali/neutral chloride waters, is also important at low pH, and is a more probable contender for the role of major complexing agent. There is some variation due to the annual seismic disturbances and seasonal changes in water levels which only affect parts of Norris Geyser Basin where rapid chemical changes

in the hydrothermal waters have been reported (Fig. 2). Many of the *REE* levels in the acid waters sampled in 1991 are lower than those same springs sampled in 1993. Hydrophane has increased levels of the *REE* – it was a neutral spring (pH 6.8) but now has a pH of 3.5. Clearwater Springs is just outside the Norris Geyser Basin in the Norris-Mammoth corridor; it has undergone a change in pH from 6 (Palmer and Sturchio, 1989) to 4 (1993 data set) without a concomitant increase in *REE* abundance. Sulphate levels are low in this spring. Geothermometry suggests that Crater Hills is sampling the deeper parts of the hydrothermal system so although the waters have pH 3.5 and reasonable levels of sulphate, mobilisation by acid-sulphate waters is not occurring here.

Conclusion

Variation in *REE* abundances is related to pH and the presence of suitable complexing agents. The low pH waters dissolve plagioclase and the *REE* from the tuffs which increases pH. Potassium is released which preferentially complexes with the sulphate ligands, consequently the fluids are less able to transport *REE*. They are consequently adsorbed onto alteration products such as clays, precipitated into sinter or incorporated into secondary minerals by exchange for H^+ on mineral exchange sites or surface adsorption.

References

- Fournier, R. O. (1989) *Ann. Rev. Earth Planet. Sci.*, 17, 13–53.
- Palmer, M. R. and Sturchio, N. C. (1989) *Geochim. Cosmochim. Acta*, 54, 2319–23.
- Wood, S. A. (1990) *Chem. Geol.*, 82, 159–186.