

LETTER

**Steric hindrance and the enhanced stability of light rare-earth elements
in hydrothermal fluids**

ROBERT A. MAYANOVIC,^{1,*} ALAN J. ANDERSON,² WILLIAM A. BASSETT,³ AND I-MING CHOU⁴

¹Department of Physics, Astronomy and Materials Science, Missouri State University, Springfield, Missouri 65897, U.S.A.

²Department of Earth Sciences, St. Francis Xavier University, P.O. Box 5000, Antigonish, Nova Scotia B2G 2W5, Canada

³Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York 14853, U.S.A.

⁴U.S. Geological Survey, MS 954, Reston, Virginia 20192, U.S.A.

ABSTRACT

A series of X-ray absorption spectroscopy (XAS) experiments were made to determine the structure and stability of aqueous REE (La, Nd, Gd, and Yb) chloride complexes to 500 °C and 520 MPa. The REE³⁺ ions exhibit inner-sphere chloroaqua complexation with a steady increase of chloride coordination with increasing temperature in the 150 to 500 °C range. Furthermore, the degree of chloride coordination of REE³⁺ inner-sphere chloroaqua complexes decreases significantly from light to heavy REE. These results indicate that steric hindrance drives the reduction of chloride coordination of REE³⁺ inner-sphere chloroaqua complexes from light to heavy REE. This results in greater stability and preferential transport of light REE³⁺ over heavy REE³⁺ ions in saline hydrothermal fluids. Accordingly, the preferential mobility of light REE directly influences the relative abundance of REE in rocks and minerals and thus needs to be considered in geochemical modeling of petrogenetic and ore-forming processes affected by chloride-bearing hydrothermal fluids.

Keywords: Petrogenetic indicators, rare earth elements, hydrothermal fluids, synchrotron radiation