

Quadrivalent praseodymium in planetary materials

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ABSTRACT

Praseodymium is capable of existing as Pr³⁺ and Pr⁴⁺. Although the former is dominant across almost all geological conditions, the observation of Pr⁴⁺ by XANES and Pr anomalies (both positive and negative) in multiple light rare earth element minerals from Nolans Bore, Australia, and Stetind, Norway, indicates that quadrivalent Pr can occur under oxidizing hydrothermal and supergene conditions. High-temperature REE partitioning experiments at oxygen fugacities up to more than 12 log units more oxidizing than the fayalite-magnetite-quartz buffer show negligible evidence for Pr⁴⁺ in zircon, indicating that Pr likely remains as Pr³⁺ under all magmatic conditions. Synthetic Pr⁴⁺-bearing zircons in the pigment industry form under unique conditions, which are not attained in natural systems. Quadrivalent Pr in solutions has an extremely short lifetime, but may be sufficient to cause anomalous Pr in solids. Because the same conditions that favor Pr⁴⁺ also stabilize Ce⁴⁺ to a greater extent, these two cations have similar ionic radii, and Ce is more than six times as abundant as Pr, it seems that Pr-dominant minerals must be exceptionally rare if they occur at all. We identify cold, alkaline, and oxidizing environments such as oxyhalide-rich regions at the Atacama Desert or on Mars as candidates for the existence of Pr-dominant minerals.

Keywords: Praseodymium, cerium, rare earth elements, oxygen fugacity, XANES, redox