

Thermodynamic modeling of REE fractionation during the interaction of monazite with chloride-carbonate fluid

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Monazite is the most abundant REE mineral, which forms in various geochemical conditions including rare metal deposits of hydrothermal and metamorphogenic type. Besides, lanthanide-actinide phosphate matrixes are very perspective for radioactive waste disposal. It is worth to reveal the trends of REE fractionation depending on physical-chemical conditions of fluid/monazite interaction.

The thermodynamic data base for lanthanide phosphates of Vieillard and Tardy (1984) as well as SUPCRT98 for aqueous species were used. A model of ideal solid solution for (Ce,La,Nd,Eu)-monazite was calculated as a first step for the following numerical experiments. The behavior of xenotime in the modeling system was used to compare the leaching ability of Y-HREE group with the LREE one. Two type of initial modeling fluid containing 4.0m NaCl + 1,5m H₂CO₃ were under attentions: acid (pH = 3.1 because of 0.1m HCl addition) and alkaline (pH = 7.3 because of 0.1m KOH addition). The following particular tasks were tested: 1) the estimation of a possible selective solubility of some LREE+Y as compared to each other during the cooling of the chloride-carbonate fluid within the 500 - 100 °C interval; 2) the calculation of the influence of fluid/REE phosphate solid phase ratio (within 10⁻⁴ – 10⁴ interval) on possible correlations between various LREE+Y in solid phases after “leaching”.

The principal results under discussion: 1) in the *acid* fluid, expected concentrations of La-, Ce- and Nd are higher by two order of magnitude as compared with the *alkaline* one; 2) the Eu-mineral of monazite demonstrates the anomalous high solubility at elevated temperatures; 3) the solubility of xenotime mineral is lower by two orders of magnitude as compared with the monazite one; 4) at low ratios of fluid/REE-phosphate intensive leaching of EuPO₄ with the following leaching of (La, Ce, Nd)PO₄ takes place with leaching of YPO₄ at the last stage of the process only.

Extensive set of new ICP-MS and XRF-SI data about REE patterns in natural monazites will be used for verification of thermodynamic models under development.

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Decoupling photochemical Fe(II) oxidation from shallow-water BIF deposition

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Oxidized Fe minerals in Archean-Paleoproterozoic banded iron formations (BIFs) are commonly taken to indicate the presence of biogenic O₂ or photosynthetic Fe(II)-oxidizing bacteria in the oceans' photic zone. However, prior to the rise of atmospheric oxygen and the development of a protective ozone layer, the Earth's surface was subjected to high levels of ultraviolet radiation. Bulk ocean waters that were anoxic at this time could have supported high concentrations of dissolved Fe(II). Under such conditions, Fe(OH)⁺ would have absorbed radiation in the 200-400 nm range, leading to the formation of dissolved ferric iron [Fe(III)], which in turn, would have hydrolyzed to form ferric hydroxide [Fe(OH)₃] at circumneutral pH. We evaluated the relative importance of photochemical oxidation using experiments that simulated the chemistry of ambient Precambrian seawater mixing with Fe(II)-rich hydrothermal fluids with, and without, UV irradiation. We found that if Fe(II) was effused from relatively shallow seamount-type vent systems directly into an anoxic photic zone, the photochemical contribution to solid-phase precipitation would have been negligible. Instead, most of the Fe(II) would have precipitated rapidly as an amorphous precursor phase to greenalite and/or siderite, depending on different simulated atmospheric pCO₂ levels. Conversely, in experiments where Fe(II) was exposed either to phototrophic Fe(II)-oxidizing bacteria or to O₂, ferric hydroxide formed rapidly, and the precipitation of ferrous iron phases was not observed. If, as suggested on mass balance grounds, BIF deposition requires that Fe be sourced from shallow seamount-type systems, then we are driven to conclude that oxide-facies BIF are the product of a rapid, non-photochemical oxidative process, the most likely candidates being direct or indirect biogenic oxidation.