

# Concentration and Aqueous Species of REE-Y in Hydrothermal Fluoride Fluids: Dependence on their T-P Parameters and Chemical Features

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There are lot of bright examples of rare earth fractionation during hydrothermal ore formation on the groups (light or heavy REE, so named tetrad-effect) or individual (Eu, Y et al.) level. In particular, REE-containing fluorite was traditionally a very popular geochemical object under study both for Russian (Barsukov et al.; Bulnaev; Smolenskiy et al.; Matveeva; Ivanova etc.) and European (Marchand; Moeller; Bau, Dulski etc.) authors. The modern thermodynamic data bases, created during the last decade, give a chance for revealing of some features and regularities of these processes. The results of estimation of rare earth speciation and their concentrations in an ore-forming fluid as a function of T-P parameters and chemical features are presented below. They have been obtained on the basis of the thermodynamic model of fluid interaction with the mixture of fluorite and eleven selected REE-Y fluorides. The software package "Hch" (Shvarov, 1999) together with the necessary thermodynamic constants for solid fluorides from Greis, Haschke (1982) and for aqueous species from Johnson et al., 1992; Haas et al., 1995; Shock et al., 1997 have been used. Five points along the way of fluid evolution were tested within 500 - 100° C temperature and 2000 bar-s.v.p. pressure interval. The most typical NaCl and CO<sub>2</sub> concentrations and acidity of the modelling fluid were selected in the accordance with the generalised results of investigation of fluid inclusions in vein quartz of different stages of formation of Iultin, Khingan (Far East, Russia) and Akchatau (Kazakhstan) Sn-W deposits (Shironosova et al., 2000). It has been established that in the case of Y and light REE (La, Ce, Pr, Nd), the first and the second fluoride complexes are the dominating REE-Y species in this fluid with a rather high (10<sup>-2</sup> mol/kg) total fluoride content. On the other hand, hydroxide complexes are the main aqueous species for the intermediate (Sm, Eu, Tb) and heavy (Yb, Lu) REE in spite of low pH=5.5 at 500 and 400° C. Neither chloride nor carbonate (+ bicarbonate) complexes have any significant role, even at very high chloride (4 mol/kg H<sub>2</sub>O) and CO<sub>2</sub> (up to 1.5 mol/kg) concentrations. At the same time, the change of fluoride REE complexes by hydroxide is possible at the low temperature part of the fluid evolution, when pH>6. There are three various groups of REE-Y from the point of view of their solubility. Eu, Yb and Sm fluorides demonstrate the most high dissolution (10<sup>-4</sup> mol/kg), when for YF<sub>3</sub> and TbF<sub>3</sub> it is close to

10<sup>-7</sup> mol/kg or lower. The solubility curves of the other selected REE fluorides (La, Pr, Nd, Ho, Lu, Yb) are located in the intermediate zone between 10<sup>-5</sup>-10<sup>-6</sup> mol/kg H<sub>2</sub>O. The position of CeF<sub>3</sub> solubility curve is sufficiently conditional because of the difference of its free energy in various literature sources. It is essential to emphasise that the solubility curves of fluorite and the majority of REE fluorides draw together during fluid evolution when pH increases. From thermodynamic point of view it can indicate less favourable conditions of REE co-precipitation and, in contrast, preferable possibilities of their leaching from fluorite lattice. More than ten years ago Sverjensky and then Wood paid their special attention to the theoretical geochemistry of Eu, Sm and Yb, i.e. to REE which can be presented in natural fluids in both +3- and +2-valence forms. Now the mentioned above maximum solubility of their fluorides looks unexpectedly, at the first glance, making this triad very mysterious. Nevertheless, the analysis of thermodynamic constants of all participants of these solubility reactions demonstrates that on the background of similar data for other REE, the free energies of solid Eu and Yb fluorides have more distinct positive deviations in comparison with those for the free energies of the dominate aqueous species (the same deviations are more shaded for SmF<sub>3</sub>, especially for its dissolved forms). Finally, the extremely low position of the solubility curve for TbF<sub>3</sub> demonstrates that the full set of HKF equation parameters for Tb aqueous species (Haas et al., 1995) should be additionally checked.

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