Experimental studies of the stability of monazite in aqueous solutions

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The solubility of monazite in aqueous solutions was investigated through experiments performed in closed reactors from 21 to 300°C. Both synthetic $NdPO_4$ and natural, Th-bearing monazite were reacted for up to 33 months with regular solution sampling to monitor the reaction progress. When equilibrium could be reached, the solubility products of $NdPO_4$ agreed within one log unit with the partial solubility product of the neodymium end-member of natural monazite. This agreement suggests that the solubility product of natural monazite can be approximated with an ideal solid-solution model. The pKs° found for this Nd end-member at 25°C (25.9) is in good agreement with previous experimental determinations of rhabdophane solubility. SEM and XPS investigations of the crystals after the experiments confirm that no rhabdophane precipitated on the monazite surfaces, however. It thus appears that the stability fields of these two minerals are very close at low temperature. Non-stoichiometric dissolutions were observed, notably for the natural monazite. Thorium, in particular, was found to reprecipitate under mildly acidic pH. This result is consistent with studies of monazite-fluid interactions occurring in nature. They show that during monazite alteration and dissolution, Th is often reincorporated in the mineral, both as a newly precipitated phase or through reincorporation in the crystalline lattice. Solubility-speciation calculations show that in the presence of fluoride, carbonate and hydroxide ligands in solution, monazite will exhibit a retrograde solubility only under acidic conditions from 70 to 300°C and to a lesser extent in neutral aqueous solutions from 150 to 300°C. When compared to the REE and P concentrations of crustal waters, these computations also suggest that monazite play an active role on the control of REE concentrations in hydrothermal fluids. These experimental and computational investigations also indicate that monazite will be extremely hard to dissolve with a granite-equilibrated groundwater, thus confirming the excellent suitability of a monazite-type ceramic for the underground long term storage of nuclear wastes.

Predicting Phosphate saturation in silicate magmas: An experimental study of the effects of melt composition and temperature

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A series of one atmosphere experiments has been performed to test the influence of iron content and oxidation state on the saturation of phosphate minerals in magmatic systems, with the aim of constraining phosphate saturation during the late stage differentiation of mafic layered intrusions. Four bulk compositions of different iron content were used. The experiments cover a range of temperatures from 1070 to 1030°C and oxygen fugacity from 1.5 log units below, to 1.5 log units above the Fayalite-Magnetite-Quartz buffer. The results demonstrate that neither iron content, nor oxidation state play a significant role on phosphate saturation. On the other hand, SiO_2 and CaO contents exert the dominant control on the appearance of a crystalline phosphate. Our results are combined with data from the literature to define an equation which predicts the molar P_2O_5 content of silicate liquids saturated in either whitlockite or apatite:

$$X_{P_2O_5}^{liq-SAT} = \exp\left[\left(T\left\{\frac{-4.653}{123.5 - X_{SiO_2}^{liq}} + 0.1207\right\}\right) - 3.333 \ln\left(X_{CaO}^{liq}\right)\right]$$

where X represents molar concentration and T is temperature in K. This equation is valid over extremely wide ranges of liquid composition and temperature (e.g. molar silica from 10 to 80%), including peraluminous liquids. The equation is used to illustrate the relative effects of melt chemistry and temperature on phosphate saturation, both in general terms and in particular for the case of ferrobasaltic differentiation. It is concluded that magmatic liquids may reach high concentrations in both phosphorus and iron, before phosphate saturation not through association of ferric iron and phosphorous, as originally postulated, but rather as a consequence of the variations of calcium and silica content of the liquid, wich is a function of magmatic differentiation. These results may help explain the petrogenesis of Nelsonites, although further work is required.