1.4.P04

SeO_4^{2-} substitution in gypsum: An experimental study

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Selenate (SeO_4^{2-}) and sulfate (SO_4^{2-}) have similar structural and chemical properties, and they can play a similar geochemical role. The competition between both anions has been considered in different fields such as sorption onto mineral surfaces [1], absorption in plants and bacteria [2, 3] and susbtitution in crystal structures [4]. However, relations between SeO_4^{2-} anion and common sulphate minerals, such as gypsum or barite have not yet been determined.

We present experimental work on crystallisation of $Ca(SeO_4,SO_4)\cdot 2H_2O$ solid solutions from aqueous solutions. Solids were synthesized at room temperature in aqueous solutions containing Na_2SeO_4, Na_2SO_4 and $CaCl_2$.

A complete structural characterization of solid solutions by X-ray powder diffraction and thermocalorimetic analysis were carried out. The presence of a miscibility gap and the differences in structural parameters and heat capacities found for the different solid compositions have allowed us to quantify the non-ideality of the solid solution and the calculation of a thermodynamic model of this solid solution-aqueous solution system.

In addition, the work includes some observations on nucleation and crystal growth in the gypsum-$CaSeO_4\cdot 2H_2O$-H_2O system. These show that the behaviour of the system is strongly influenced by the relatively high solubility of the $CaSeO_4\cdot 2H_2O$ endmember compared with gypsum. The results are generally consistent with the behaviour of selenate in the presence of gypsum in nature.

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1.4.P05

Incorporation of trivalent Actinides (Cm(III)) in calcite: A Time Resolved Laser Fluorescence Spectroscopy (TRLFS) study

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Incorporation of radionuclides into the bulk structure of a mineral phase represents a very important retardation process, but very little is known about the reaction mechanisms and the involved incorporated species. The common occurrence of calcium carbonate at localities impacted by radionuclide waste has focused attention on the effectivness of calcite in the retention of actinides. Moreover carbonates are among the most important secondary alteration products formed during the degradation of cement in radioactive waste repositories. Previous studies have shown that REE are strongly partionned into calcite [1]. Cm(III) interaction with calcite in the trace concentration was also investigated by TRLFS [2].

In order to characterize and quantify the substitution of Ca(II) by Cm(III) (coordination, charge compensation), we synthesized homogeneous Cm(III) coprecipitated calcite in a stirred-flow-through experiment. Flow-Through Reactors are of great interest because they allow crystal growth under constant and controlled conditions (saturation state, pH, ionic strength).

Two calcites, with different Cm(III) concentrations (0.5 nM Cm^{3+} and 500nm M^{3+} (0.5 nm Cm^{3+} and 455,5 nM Gd^{3+})) were grown and investigated by TRLFS. The spectra of both calcites show the same two emission bands at 605.5 nm (1) and 620 nm (2), which can be assigned to two different Cm(III)/calcite species. The proportion of the first species (1) increases with increasing concentration of M^{3+} in the reacting solution. Fluorescence emission lifetime measurements show two Cm(III) species with two different lifetimes for both Cm(III)/calcites. The first species (1) has a lifetime of $\tau = 350$ µs and the second species a lifetime of $\tau = 2167$ µs. According to the linear correlation [3] between the lifetime of the excited state and the water or OH^- molecules in the first coordination sphere of the Cm(III) species, both lifetimes indicate that Cm(III) is incorporated into the calcite bulk structure. A lifetime of 350 µs correlates with one water or OH^- molecule in the first coordination sphere. A lifetime of 2167µs indicates the total loss of the hydration sphere.

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