Arsenic removal by gypsum and calcite: the continuum between sorption and solid-solution phenomenon

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Results and Discussion

The reactions developed during As (III or V) uptake by calcite and gypsum from aqueous solution were characterised by solubility and X-Ray and Neutron Diffraction structural studies. As-containing solids (calcite and gypsum) were grown from room-temperature supersaturated aqueous solutions doped with As(III) and As(V), respectively.

Solubility data (Fig 1 a, b) shows a continuum between sorption and formation of solid-solutions (Ca(SO_4,$HAsO_4$) and Ca(CO_3, $HAsO_3$).

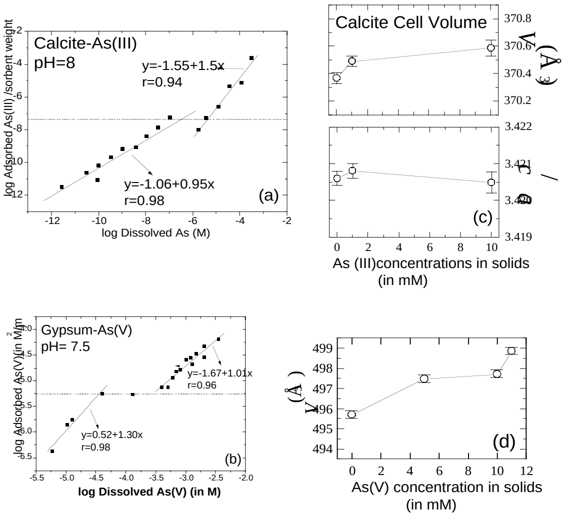

Fig. 1: a, b) Adsoption isotherms; **c, d)** cell volume vs. As contents

By means of Rietveld refinement of X-Ray and Neutron diffraction spectra, we have obtained unit cell volumes of these solid-solutions to vary with arsenic contents. This dependence is weak for As(III) incorporation in calcite (Fig. 1c) but strong for As(V) incorporation into gypsum (Fig. 1 d). Calcite and gypsum are therefore adequate sinks for arsenic in calcium rich sites under alkaline and acid conditions, respectively. The long-term stability of these solids solutions needs further studies.

Effect of metamorphic reaction history on isotopic dating of minerals

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Metamorphism of the Saxon Granulite Massif (SGM) culminated in P-T conditions in the range of 22 kbar and 1050°C and ceased under rapid exhumation to the middle crust and subsequent cooling within a few million years after the metamorphic peak (Romer and Rötzler, 2001). The fast exhumation and cooling should reduce the possibility of post-crystallization diffusional loss of in situ formed radiogenic isotopes. Ultrahigh-temperature (UHT) metamorphism should favor isotopic homogenization among both reactant and product minerals of the metamorphic reactions. Initial isotopic heterogeneity among metamorphic product minerals would indicate that even at UHT isotopic homogenization is not reached and that sequential metamorphic reaction is a poor process to homogenize the isotopic composition. Consequently, it is even less likely that isotopic homogenization is reached at lower metamorphic grade.

The closely spaced samples from the SGM passed together the same P-T conditions, but developed contrasting mineral assemblages due to different bulk rock composition. Dating the same metamorphic minerals in the various samples should yield for one mineral the same age in all samples. If the corresponding mineral ages among the various samples differ by an amount larger than the duration of the entire metamorphic cycle, this difference could arise only from the reaction history of these rocks. The geochronologically relevant elements are redistributed among remaining reactants and reaction products during metamorphism. Subsequent reactions involve different reactants, i.e., a different subvolume of the rock, and the isotopic composition of the reaction products is likely to be different from earlier formed product minerals. Thus, the sequence of metamorphic reactions does not result in isotopic homogenization.

Our analytical results imply that contrasting ages obtained by different geochronological systems (U-Pb, Sm-Nd, Rb-Sr) or on different metamorphic minerals not necessarily reflect (1) contrasting closure behavior of these minerals or (2) highly contrasting diffusion rates among the elements used for dating, but rather represent the effect of heterogeneous initial isotopic composition of Pb, Nd, and Sr due to the reaction history.

References

Romer R.L. and Rötzler J. (2001) *J. Petrol.* **42,** 2015-2032.