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The effect of supersaturation rate on the composition of carbonate solid solutions

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Background

Recent work on the precipitation of binary solid solutions has shown that the partitioning of metals of environmental interest into the solid solution is decreased when the solid solution precipitates from supersaturated aqueous solutions [1]. For example, experiments in Si-gels from this study on the $(Cd,Ca)CO_3$ solid solution show that the partitioning of Cd to the solid phase is decreased by up to 20%. These results have important implications for the mobility of metals in the environment. and for studies that use the partitioning of metals (e.g. Sr^{2+}) into carbonates to infer paleoclimatic conditions.

In addition to the effect of supersaturation it has also been shown that the partioning behaviour of metals is also affected by the rate at which supersaturation is achieved [2].

Furthermore, this change in partitioning behaviour with supersaturation and supersaturation rate can be predicted using a model based on the beta saturation function and the classical nucleation rate equation [3].

This study

This work has studied the effect of supersaturation and supersaturation rate on the composition of $(M,Ca)CO_3$ solid solutions (M = Ba, Cd, Co, Mn or Sr) precipitating from aqueous solutions. This effect is assessed using two types of experiments that allow variation in the supersaturation rate: "hanging drop" experiments and Si-gel experiments.

The results are then compared with the predictions of the theoretical model [3].

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Geochemistry of cadmium in sphalerite from Creede, CO, USA: A tool to study fractionation in hydrothermal systems

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Geochemical process modeling has become an important tool to decipher and present problems in earth sciences. Yet there are few instances in which the models have been critically compared with field observations.

To do this, electron microprobe traverses (with 10 μm steps) wer made across coarse, growth-zoned sphalerite crystals from the much-studied OH vein in the Creede district. Zn, Cd, Fe and Mn were analyzed from 5 sample localities representing an area of 300 m along the vein and 150 meters in depth, and fluid inclusion temperatures and equivalent NaCl salinities that characterize each traverse were measured. In contrast to Fe and Mn which may reside in several different minerals, Zn and Cd reside only in sphalerite. Therefore, by studying the Cd/Zn fractionation and comparing the results with the salinity and temperature of the depositing fluid, one may test models for sphalerite precipitation.

Distinctive composition patterns are correlative between the different samples, even hundred of meters apart, although the Cd level shifts. The trend in the shift in space consists of a general increase in the Cd concentration in sphalerite upwards and towards the southern (distal) part of the orebody. Cd in sphalerite has a negative correlation with temperature and salinity of the hydrothermal fluids within each growth zone indicating that, in agreement with the equilibrium constants for chloride complexes for Zn and Cd, as the solutions cool and also become diluted, Cd is more strongly fractionated from solution to crystals than is Zn. More comprehensive modeling is in progress.

This study promises to help us understand the mechanisms of fractional crystallization in hydrothermal systems and, therefore, processes of ore formation.

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