The effect of $[Ba^{2+}]/[SO_4^{2-}]$ ratio on the mechanism of barite growth at constant supersaturation

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We investigated the mechanism of barite growth in a fluid cell of an Atomic Force Microscope by passing solutions of constant supersaturation (Ω) but variable $[Ba^{2+}]$ to $[SO_4^{2-}]$ ratio over a barite substrate. We observed that the potential for two-dimensional nucleation increases with increasing $[Ba^{2+}]/[SO_4^{2-}]$ ratio and the mechanism of crystal growth changes from advancement of pre-existing steps to massive island spreading as the cation:anion ratio increases.

Experiments were carried out at two different degrees of supersaturation (7.2 and 12.6) with $[Ba^{2+}]/[SO_4^{2-}]$ ratios varying over several orders of magnitude. We observed advancement of pre-existing cleavage steps to be responsible for crystal growth for $[Ba^{2+}]/[SO_4^{2-}]$ ratios up to 0.25, while two-dimensional nucleation was not observed. At higher cation:anion ratio two-dimensional nucleation occurs with the island density generally increasing with increasing cation concentration in solution.

The results suggest that the rate limiting factor for two-dimensional nucleation to occur is the frequency of cation attachment, which is determined by the barrier for cations to approach the surface. We carried out further experiments using water-methanol mixtures for the growth solution to corroborate the hypothesis that the solvation water of the crystal surface and of the cation effectively hinders the ability of the cation to reach the surface and that desolvation is the rate-limiting kinetic process in crystal growth. Massive island nucleation was observed on the barite surface in contact with water/methanol solutions with $[Ba^{2+}]/[SO_4^{2-}]$ ratio two orders of magnitude lower than 0.25 (while adjusting the ion concentration to the desired Ω in the solvent mixture). Step advancement and island-spreading velocity also changes with varying cation to anion ratio with the tendency to reduce growth velocity while moving towards extreme values of ion ratio.

Our findings show that barite crystal growth under the same supersaturation conditions occurs by different mechanisms with the cation adsorption on the surface being the rate limiting factor for two-dimensional nucleation. This conclusion is relevant in considering natural systems where crystals grow from solutions of highly variable stoichiometry.

Distribution of Platinum- group element and minerals within the chromitites of Tauride Ophiolite Belt (Pozantı-Karsantı, Pınarbaşı, Mersin), Southern Turkey

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The Tauride Ophiolite Belt was emplaced in southern Turkey. Total bulk platinum group element (PGE) concentrations of chromitites from the Pınarbaşı area range from 67.5 to 253 ppb. The total bulk PGE values of Pozantı-Karsantı chromitites are between 38.2-2730 ppb. The PGE distribution of Tauride chromitites exhibits a negative slope in chondrite normalised diagram. Their Pd/Ir ratio is between 0.01-0.95 which may reflect a magma source which has a severely depleted character. Although most of the chromitite samples from the Tauride Ophiolite Belt have negative slopes in chondrite normalised diagrams, one of the samples from the Pozantı-Karsantı ophiolite is unexpectedly PPGE-enriched (Rh: 150; Pt: 1390 ve Pd: 832 ppb) and has a positive slope in the normalised chondrite diagram. The PPGE values of the chomitites from Pozantı-Karsantı are recorded in the literature as one of highest determined PGE values of chromitites in Turkey (Kozlu-Erdal and Melcher, 2006). The primary PGM inclusions (Pınarbaşı) are laurite, Ir-sulphide, cuproiridsite, Ru-Os (Pozantı-Karsantı) alloys and Os-Ir alloys (Mersin) (Kozlu-Erdal and Melcher, 2007).

Conclusions

The geochemical character of chromitites from Tauride ophiolites and their PGE and PGM composition reflect crystallization from severely depleted boninitic magmas in the supra-subduction zone.

References

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