

Uncovering the mysteries of (Ba, Sr)SO₄ formation in ocean: Heterogeneous (Ba, Sr)SO₄ nucleation on organics

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Marine barite cycling can be used for reconstructing paleoenvironments. However, the geological records showing extensive occurrence of marine barite in undersaturated seawater remains paradoxical. Furthermore, Sr enrichment in some marine barites is not interpreted within the current framework of solid solution growth. Here we report the promoted (Ba_xSr_{1-x})SO₄ formation on mixed thiol (-SH) and carboxyl (-COOH) coated substrates from undersaturated bulk solution. Real-time observation of (Ba_xSr_{1-x})SO₄ formation kinetics reveals that small (Ba_xSr_{1-x}) SO₄ nuclei (~ 2-4 nm) formed at water-organic interfaces; while big (~ 5 μm) crystals formed in bulk solution. The strong attraction of cation ions (e.g. Ba²⁺ and Sr²⁺) towards the organic surfaces leads to much higher supersaturation in the local solution at water-organic interfaces, and therefore promotes heterogeneous (Ba_xSr_{1-x})SO₄ nucleation on the organics. The precipitates in bulk solution were Ba-dominant ($x \approx 1$), due to the lower solubility of BaSO₄ over SrSO₄, consistent with solid solution growth predictions. The (Ba_xSr_{1-x})SO₄ precipitates at organic-water interfaces are enriched with Sr (e.g., $1-x = 0.28-0.93$), attributed to lower interfacial energy of SrSO₄ (0.097 J/m²) than that of BaSO₄ (0.125 J/m²), consistent with predictions of solid solution nucleation. Insights from this study provides plausible explanations for marine barite formation in oceans, as well as for the enrichment of Sr in some marine barites.