

## Solubility of Na<sub>2</sub>SO<sub>4</sub> in silica-saturated solutions: Implications for REE mineralization

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### ABSTRACT

Sulfate is traditionally considered to have retrograde solubility in aqueous solutions. However, our recent hydrothermal diamond-anvil cell (HDAC) experiments have shown that the solubility of Na<sub>2</sub>SO<sub>4</sub> changes from retrograde to prograde in the presence of silica, leading to the formation of sulfate-rich solutions at high temperatures, in line with observations on natural geofluids. In this study, we use synthetic inclusions of fused silica capillary capsules containing saturated Na<sub>2</sub>SO<sub>4</sub> solutions and Na<sub>2</sub>SO<sub>4</sub> crystals to quantitatively investigate the solubility of Na<sub>2</sub>SO<sub>4</sub> at different temperatures in the Na<sub>2</sub>SO<sub>4</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. Sulfate concentrations were measured using Raman spectroscopy and calibrated using Cs<sub>2</sub>SO<sub>4</sub> solutions with known concentrations. The solubility of crystalline Na<sub>2</sub>SO<sub>4</sub> dropped slightly when heated from 50 to 225 °C and dramatically from 225 to 313 °C. At 313 °C, the Na<sub>2</sub>SO<sub>4</sub> crystals began to melt, forming immiscible sulfate melt coexisting with the aqueous solution, with or without solid Na<sub>2</sub>SO<sub>4</sub>. With the formation of sulfate melt, the solubility of Na<sub>2</sub>SO<sub>4</sub> was reversed to prograde (i.e., solubility increased considerably with increasing temperatures). The solubility of Na<sub>2</sub>SO<sub>4</sub> in the measured solution was significantly higher than that predicted in the absence of SiO<sub>2</sub> over the entire temperature range (except for temperatures around 313 °C). This indicates that the presence of SiO<sub>2</sub> greatly changes the dissolution behavior of Na<sub>2</sub>SO<sub>4</sub>, which may be caused by the formation of a sulfate-silicate intermediates such as Si(OH)<sub>4</sub>SO<sub>4</sub><sup>2-</sup>. Considering that most crustal fluids are silica-saturated, the solubility curve of Na<sub>2</sub>SO<sub>4</sub> obtained in this study can better reflect the characteristics of geofluids when compared to that of Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O binary system. At temperatures of 313–425 °C, the solubility of Na<sub>2</sub>SO<sub>4</sub> increases with temperature following the function  $C_{\text{sulfate}} = -3173.7/T + 5.9301$ , where  $C_{\text{sulfate}}$  and  $T$  represent the solubility of Na<sub>2</sub>SO<sub>4</sub> in mol/kg H<sub>2</sub>O and temperature in Kelvin, respectively. As an application, this temperature-solubility relationship can be used to evaluate the sulfate contents in fluid inclusions that contain sulfate daughter minerals, based on the temperature of sulfate disappearance obtained from microthermometric analysis. The sulfate concentrations of the ore-forming fluids of the giant Maoniuping carbonatite-related rare earth element (REE) deposit (southwest China) were calculated to be 4.67–4.81 *m* (mol/kg H<sub>2</sub>O). These sulfate concentrations were then used as internal standards to calibrate the previously reported semi-quantitative results of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis of REE-forming stage fluid inclusions at this deposit. The calculated Ce concentrations in the REE-mineralizing fluid range from 0.42 to 0.49 wt%. The high fluid REE contents suggest that the sulfate-rich fluids are ideal solvents for REE transport. A mass-balance calculation was carried out to evaluate the minimal volume of carbonatite melt that was required for the formation of the giant Maoniuping REE deposit. The result indicates that the carbonatite dikes in the mining area are enough to provide the required fluids and metals, and thus a deep-seated magma chamber is not necessary for ore formation.

**Keywords:** Na<sub>2</sub>SO<sub>4</sub> solubility, silica saturation, rare earth element, mineralizing fluid, FSCC