Forming sulfate- and REE-rich fluids in the presence of quartz

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INTRODUCTION

Sulfate is ubiquitous in Earth and terrestrial planets or moons such as Mars and Europa (McCord et al., 1998; Chipera and Vaniman, 2007; Debret and Sverjensky, 2017). As a potential agent for oxidation and a ligand for metal complexation, sulfate may play an important role in ore formation and planet-scale matter circulation. In particular, the sulfate ion, as a hard Pearson base (Railsback, 2003), forms strong bonds with hard acids such as rare earth elements (REEs)(III; trivalence) in hydrothermal solution (Liu et al., 2017). Nevertheless, metal complexation is controlled not only by the stability of the complex, but also the ligand’s availability, which should, based on our current knowledge, be poor for sulfate ions due to the retrograde solubility (i.e., decreasing with increasing temperature; Seward et al., 2014) of sulfate minerals. Previous experiments in quartz-absent conditions also showed very limited REE solubility in sulfate-bearing fluids at elevated temperatures because of the insoluble nature of REE-sulfate salts (Migdisov et al., 2006). However, sulfate-rich fluids are observed in natural geofluids (Pasteris et al., 1996), and they have proved to be capable of dissolving large amounts of REEs (Xie et al., 2015). Furthermore, sulfate-rich inclusions containing 70–75 vol% of sulfate daughter minerals at the Liuzhuang REE deposit and the world-class Maochuan REE deposit (in Sichuan, China) present unusual phase transitions upon heating, showing melting of the daughter minerals at ~330 °C (immiscible melt and fluid) and total homogenization to a sulfate-rich aqueous fluid at ~450 °C via dissolution of the sulfate melt (Xie et al., 2015). These observations contradict the retrograde solubility of sulfate salts. In the case of Na2SO4(s) (solid sodium sulfate), its solubility is predicted to be ~10 wt% at 400 °C and 200 MPa based on the currently available thermodynamic data, which is significantly lower than that at ambient condition (~33 wt% at 32 °C).

The “unexpected” behavior of sulfate in geofluids can be explained by the complexity of natural systems, since sulfates may behave differently in multicomponent systems than in the water-sulfate binary. An example is the solubility of anhydrite in NaCl-H2O solutions, which is much higher than that in pure water (Newton and Manning, 2005). More intriguingly, previous studies have shown that silica-saturated sulfate solutions contain significant amounts of sulfate-silica complexes (Marshall and Chen, 1982; Schmidt, 2009; Wang et al., 2016) and show complex phase transitions (coexistence of three or more immiscible liquids) upon heating (Kotel’nikova and Kotel’nikov, 2010), suggesting that quartz, a ubiquitous mineral in the crust, may also influence the solubility and phase relationships in sulfate-water systems. Here, we show that the presence of quartz switches the solubility of Na2SO4 and Nd4(SO4)3 from retrograde to prograde at temperatures typical of hydrothermal REE mineralization, thus significantly changing the behavior of the sulfate-water systems.

RESULTS AND DISCUSSION

To explore the high-temperature behavior of quartz-saturated sulfate-water systems and to evaluate their ability to transport REEs, we conducted hydrothermal diamond anvil cell (HDAC; Bassett et al., 1996) experiments on the Na2SO4-SiO2-H2O and Na2SO4-Nd4(SO4)3-SiO2-H2O systems. Sulfate crystal(s) of [Na2SO4(s) ± Nd(SO4)3(s)], a sulfate-saturated solution, and quartz were loaded as starting materials (Figs. 1a and 2). In several runs, only mirabilite [Na2SO4·10H2O(s)] and quartz were loaded, so that the bulk Na2SO4/H2O molar ratio (0.1) was known.

Forming “Low-Temperature” Na2SO4 Melt in the Presence of Quartz

In the Na2SO4-SiO2-H2O system, Na2SO4(s) melted at ~270 °C (Fig. 1); this is nearly 200 °C lower than the water-saturated melting
temperature of pure Na$_2$SO$_4$ ($\sim$450 °C; Valyashko, 2008). Quick cooling of the sample locally preserved the melt as amorphous sulfate, but most melt recrystallized quickly in the presence of water (Fig. 3A). In order to “freeze” the molten sulfate, a tiny leak was applied to the sample chamber prior to quenching in order to expel water at high temperature, allowing the melt to be preserved as “glassy” sulfate under dry conditions during quenching. Sulfate melt quenched using this method is characterized by a “foamy” structure that is similar to volcanic pumice (Fig. 3B), indicating that the melt was rich in water.

Compositional analysis using energy dispersive spectrometry showed that minor (a few tenths of weight %) silica was incorporated into the sulfate melt, possibly via the formation of sulfate-silicic compounds such as Si(OH)$_3$SO$_4^−$,

as proposed by Marshall and Chen (1982). The amount of silica present in the melt was similar to its solubility in the Na$_2$SO$_4$ solution ($\sim$0.1 wt% in 1.6 molal Na$_2$SO$_4$ solution at 300 °C; Marshall and Chen, 1982). The amorphous sulfate containing minor silica, instead of stoichiometric Na$_2$SO$_4$, further indicates that it was quenched melt rather than an aggregation of tiny Na$_2$SO$_4$ crystals. In situ Raman spectra revealed that the sulfate melt was mainly composed of monodentate Na$^+$-SO$_4^{2−}$ ion pairs or polymers (Rudolph et al., 1999), with subordinate free SO$_4^{2−}$ ions and molecular water (Fig. DR1 in the GSA Data Repository$^1$). Silicon-oxygen vibration modes were not detected, possibly due to the low content of silica in the melt.

### Elevated Na$_2$SO$_4$(s) Solubility at High Temperatures

Na$_2$SO$_4$ solubility shows an inversion in trend upon heating: Solubility is retrograde at temperatures $<\sim$270 °C [evidenced by overgrowth of Na$_2$SO$_4$(s) crystals] and prograde at higher temperatures (dissolution of sulfate melt into the aqueous solution).

The key transition at $\sim$270 °C is coupled with the initiation of Na$_2$SO$_4$(s) melting. The linkage between sulfate melting and solubility change can be simply explained by the difference in the formation enthalpies of Na$_2$SO$_4$(s) and sulfate melt, and thus the temperature dependence (i.e., signs of enthalpy changes) of the two solubility-controlling reactions [dissolution of Na$_2$SO$_4$(s) and sulfate melt].

Prograde dissolution of sulfate melt leads to the formation of a homogeneous sulfate-rich solution at $\sim$330 °C. In runs using mirabilite as the starting material, a homogeneous fluid with 42.8 wt% Na$_2$SO$_4$ was eventually formed upon disappearance of the sulfate melt (Fig. 1). Free SO$_4^{2−}$ ions were the only detectable sulfate species in the homogenized fluid (Fig. DR1), indicating that the condensed liquid was a sulfate-rich aqueous solution rather than a water-rich melt at the molecular level.

The diagram of Figure 1 was established with a single bulk Na$_2$SO$_4$/H$_2$O ratio (42.8 wt% Na$_2$SO$_4$). To evaluate the influence of bulk composition, several experiments with higher but unknown bulk Na$_2$SO$_4$ contents were carried out by loading a quartz piece, mirabilite, and

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$^1$GSA Data Repository item 2020043; supplementary information on methods, is available online at http://www.geosociety.org/databook/2020/, or on request from editing@geosociety.org.
an anhydrous Na$_2$SO$_4$(s) crystal as starting materials. In the more concentrated systems, sulfate still dissolved, albeit at higher temperatures (up to ~450 °C, see the Data Repository and Table DR1), suggesting that sulfate should be highly mobile in high-temperature geofluids.

**Sulfate-Rich Fluid as an Efficient Solvent for REE Mobilization**

To investigate REE transportation in sulfate-rich fluids, we carried out experiments in the Na$_2$SO$_4$-Nd$_2$(SO$_4$)$_3$-SiO$_2$-H$_2$O system (Fig. 2). Again, the presence of silica changed the dissolution behavior of Nd$_2$(SO$_4$)$_3$ significantly. In the quartz- and water-saturated system, melting of the eutectic Na$_2$SO$_4$-Nd$_2$(SO$_4$)$_3$ system led to the formation of a Na-Nd-sulfate melt, evidenced by the presence of Nd (~20 wt%) in the quenched melt (Fig. 3C). Similar to Na$_2$SO$_4$, the melt-borne Nd showed prograde solubility, and the loaded Nd$_2$(SO$_4$)$_3$ completely dissolved into the solution at ~420 °C (Fig. 2), forming a sulfate- and REE-rich fluid similar to the observations in natural inclusions (Xie et al., 2015).

To confirm the role of quartz in stabilizing sulfate melt and thus maintaining the sulfate- and REE-rich fluids, experiments were carried out in quartz-absent Na$_2$SO$_4$-Nd$_2$(SO$_4$)$_3$-H$_2$O and Na$_2$SO$_4$-H$_2$O systems. Through the whole temperature range, both Na$_2$SO$_4$(s) and Nd$_2$(SO$_4$)$_3$(s) remained in the solid state and showed retrograde solubility (overgrowth of the crystals) upon heating, resulting in sulfate- and REE-poor solutions at high temperatures (Fig. DR2).

In earlier models of REE mineralization (e.g., Williams-Jones et al., 2000), REE(III)-fluoride complexes were believed to be predominant due to their great stability at elevated temperatures (orders of magnitude greater than those of chloride complexes). More recent studies concluded that the weaker chloride complexes predominate in brines, because the availability of the fluoride ion is poor in geofluids (Migdisov and Williams-Jones, 2014; Xing et al., 2019). The current paradigm proposes that both chloride and sulfate are potential ligands for REE(III) transport (Migdisov et al., 2016). Our experimental results prove that sulfate can have very high availability in quartz-saturated crustal fluids, and the presence of quartz will prevent the precipitation of REE-sulfate solids. Given the strong stability of aqueous REE-sulfate complexes (with formation constants close to those of REE-fluoride complexes; Migdisov et al., 2016), the sulfate ion is indeed a favorable ligand for REE transport.

The predominance of REE(III)-sulfate complexes is further confirmed by thermodynamic simulations, which calculated the solubility of monazite-(Nd) in F$^-$, Cl$^-$, and sulfate-bearing fluids from 300 °C to 500 °C. In a quartz-absent environment, in which sulfate salts will precipitate at high temperatures, REE-sulfate complexes are negligible in the fluid (Fig. 4A). More importantly, this fluid has very limited ability to transport Nd (~10$^{-3}$ ppm; Fig. 4C) and can hardly account for ore formation, even if REE-carbonate minerals (e.g., bastnaesite) may have greater solubility than monazite-(Nd). The silica-induced solubility change cannot be directly calculated because the thermodynamic properties of sulfate melts and aqueous sulfate-silicic compounds are unknown. However, the major effect of adding quartz to a system is to increase sulfate solubility, and this can be simulated simply by preventing the precipitation of sulfate salts (see the Data Repository). In the presence of quartz, the sulfate-rich fluid will be fertile for REE mineralization, containing up to 50 ppm of Nd, predominantly in the form of Nd-sulfate complexes (Figs. 4B and 4C). The Na$_2$SO$_4$ concentration in the model fluid (2 mol/kg H$_2$O) was lower than that in natural ore-fluids (Xie et al., 2015), a choice imposed by the limitations of available activity coefficients models. Therefore, the calculated REE concentrations are likely to underestimate the REE-carrying capacity of natural fluids. In
any case, our experimental results and simulations show that sulfate-rich fluids can account for the formation of the REE-rich ore fluids at the Mao-niuiping and Lizhuang deposits, where quartz is present accompanying REE minerals (Xie et al., 2015). Given the common occurrence of sulfate minerals in carbonatite-related REE deposits (Fan et al., 2016; Olson et al., 1954; Xu et al., 2015), we infer that the sulfate ion may indeed be the major ligand responsible for hydrothermal-magmatic REE mineralization worldwide.

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