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) (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 sulfate-REE-bearing complexes (Migdiss, 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 Liuzhung REE deposit and the world-class Mawu 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 sulfate-saturated fluids contain significant amounts of sulfate-silica complexes (Marchall and Chen, 1982; Schmidt, 2009; Wang et al., 2016) and show complex phase transitions (coexistence of three or more immiscible liquids) upon heating (Kotel’nikov 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) ± Nd₄(SO₄)₃(s)], a sulfate-saturated solution, and quartz were loaded as starting materials (Figs. 1 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 point of Na₂SO₄. Melt inclusions in feldspar from carbonatite-related rare earth element (REE) deposits are known for their retrograde solubility, implying that they should be insoluble in high-temperature geofluids. Here, we show that the presence of quartz can significantly change the dissolution behavior of Na₂SO₄, leading to the formation of extremely sulfate-rich fluids (at least 42.8 wt% Na₂SO₄) at temperatures ~330 °C. The elevated Na₂SO₄ solubility results from prograde dissolution of immiscible sulfate melt, the water-saturated solidus of which decreases from ~450 °C in the binary Na₂SO₄-H₂O system to ~270 °C in the presence of silica. This implies that sulfate-rich fluids should be common in quartz-saturated crustal environments. Furthermore, we found that the sulfate-rich fluid is a highly effective medium for Nd mobilization. Thermodynamic modeling predicts that sulfate ions are more effective in complexing REE(III) than chloride ions. This reinforces the idea that REEs can be transported as sulfate complexes in sulfate-rich fluids, providing an alternative to the current REE transport paradigm, wherein chloride complexing accounts for REE solubility in ore fluids.

ABSTRACT
The presence of sulfate-rich fluids in natural magmatic hydrothermal systems and some carbonate-related rare earth element (REE) deposits is paradoxical, because sulfate salts are known for their retrograde solubility, implying that they should be insoluble in high-temperature geofluids. Here, we show that the presence of quartz can significantly change the dissolution behavior of Na₂SO₄, leading to the formation of extremely sulfate-rich fluids (at least 42.8 wt% Na₂SO₄) at temperatures ~330 °C. The elevated Na₂SO₄ solubility results from prograde dissolution of immiscible sulfate melt, the water-saturated solidus of which decreases from ~450 °C in the binary Na₂SO₄-H₂O system to ~270 °C in the presence of silica. This implies that sulfate-rich fluids should be common in quartz-saturated crustal environments. Furthermore, we found that the sulfate-rich fluid is a highly effective medium for Nd mobilization. Thermodynamic modeling predicts that sulfate ions are more effective in complexing REE(III) than chloride ions. This reinforces the idea that REEs can be transported as sulfate complexes in sulfate-rich fluids, providing an alternative to the current REE transport paradigm, wherein chloride complexing accounts for REE solubility in ore fluids.

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temperature of pure Na$_2$SO$_4$ (~450 °C; Vyalys-
hko, 2008). Quick cooling of the sample locally
preserved the melt as amorphous sulfate, but
most melt recrystallized quickly in the pres-
ence 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 disper-
sive 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$_4^{2-}$,
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 (~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 stoic-
chometric 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
the presence of sulfate melt at the molecular level.

Figure 2. Hydrothermal diamond anvil cell (HDAC) experiment results of Na$_2$SO$_4$-Nd$_2$(SO$_4$)$_3$-SiO$_2$-
H$_2$O system. Mirabilite, Nd$_2$(SO$_4$)$_3$-8H$_2$O(s), and a quartz piece were loaded as starting materials. Hydrated sulfates are fine-grained and almost opaque under the microscope, and thus phase
relationships are shown from 209 °C, after their dehydration. Nd$_2$(SO$_4$)$_3$(s) and Na$_2$SO$_4$(s) started
to dissolve into aqueous solution after formation of sulfate melts, and homogenous Nd- and
sulfate-rich fluid was formed at 416 °C. V—vapor bubble; Q—quartz; Aq—aqueous solution; M—sulfate melt; L—homogenized fluid.

(1/10). Phase diagram was established from results of five runs of HDAC experiments with the same bulk Na$_2$SO$_4$/H$_2$O ratio but different bulk densities, which determine the dP/dT (P—pressure; T—temperature) ratios of isochoric systems. Polymorphs of Na$_2$SO$_4$(s) were determined by Raman spectra (Fig. DR1 [see footnote 1]); the presence of sulfate melt was determined by both optical observation (e.g., Fig. DR3) and Raman spectroscopy (Fig. DR1). Incipient melting of sulfate is hard to identify, but it can be verified by the presence of amorphous sulfate after quenching (Fig. DR4), and it was confirmed that initial melting of Na$_2$SO$_4$(s) is coupled with transition from type III to type I polymorphs. Repeated cycles of heating and cooling were conducted during run using gold-lined gasket to confirm that diagram represents stable assem-
blages (see the Data Repository [see footnote 1]). V—vapor bubble; Q—quartz; Aq—aqueous solution; M—sulfate melt; L—homogenized fluid.

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 ~<270 °C [evidenced by over-
growth of Na$_2$SO$_4$(s) crystals] and prograde at higher temperatures (dissolution of sulfate melt into the aqueous solution).

The key transition at ~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 ~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),
demonstrating that the condensed liquid was a sulfate-
rich aqueous solution rather than a water-rich
melt at the molecular level.

The diagram of Fig. 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 com-
position, several experiments with higher but
unknown bulk Na$_2$SO$_4$ contents were carried out
by loading a quartz piece, mirabilite, and
Sulfate-Rich Fluid as an Efficient Solvent for REE Mobilization

To investigate REE transportation in sulfate-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 great 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 (Fig. 4). In a quartz-absent environment, in which sulfate salts will precipitate at high temperatures, REE-sulfate complexes are neglectable in the fluid (Fig. 4A). More importantly, this fluid has very limited ability to transport Nd ($\sim$10$^{-10}$ 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
Figure 4. Results of thermodynamic simulation, showing speciation of aqueous Nd in quartz-absent (A) and quartz-saturated (B) systems, and comparison of solubility of monazite-Nd (C) shown as total dissolved Nd (C). Simulations were carried out in an Na-Nd-Ca-S-P-F-C-O-H system at 150 MPa. CO$_2$-bearing solutions contained 2 molal Na$_2$SO$_4$ and NaCl, respectively, and were in equilibrium with monazite-Nd), fluorite,apatite, and calcite. For simplicity, only predominant species of each type of aqueous Nd complex (chloride, fluoride, carbonate, hydroxide, and sulfate) are shown. For example, Na$_2$SO$_4$Nd$^{3+}$ predominates over NaNdSO$_4^+$, and so latter is not shown in the figure.

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