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Calcium isotope systematics at hydrothermal conditions: Mid-ocean ridge vent fluids and experiments in the $CaSO_4$-NaCl-H_2O system

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Abstract

Two sets of hydrothermal experiments were performed to explore Ca isotope fractionation and exchange rates at hydrothermal conditions (410–450 °C, 31.0–50.0 MPa). The first set of experiments determined the magnitude of vapor-liquid Ca isotope fractionation and anhydrite solubility in the $CaSO_4$-NaCl-H_2O system. The data indicate no statistical difference between the Ca isotopic composition of coexisting vapor and liquid. The second set of experiments utilized an anomalous ^{43}Ca spike to determine the rate of Ca exchange between fluid and anhydrite as a function of total dissolved Ca concentration. Results show that the rate of exchange increases with dissolved Ca concentrations (12–23 mM/kg), but no change in exchange rate is observed when the Ca concentration increases from 23 to 44 mM/kg Ca. 74–142 days are required to achieve 90% anhydrite-fluid Ca isotope exchange at the conditions investigated, while only several hours are necessary for vapor-liquid isotopic equilibrium. The lack of vapor-liquid Ca isotope fractionation in our experiments is consistent with $\delta^{44}Ca$ of mid-ocean ridge hydrothermal vent fluids that remain constant, regardless of chlorinity. Moreover, the narrow range of end member fluid $\delta^{44}Ca$, −0.98 to −1.13‰ (SW), is largely indistinguishable from MORB $\delta^{44}Ca$, suggesting that neither phase separation nor fluid-rock interactions at depth significantly fractionate Ca isotopes in modern high-temperature mid-ocean ridge hydrothermal systems.

Keywords: Mid-ocean ridge; Hydrothermal; Calcium isotopes; Anhydrite; Phase separation; Isotope exchange

1. INTRODUCTION

High temperature hydrothermal systems at mid-ocean ridges play an important role in determining the chemical and isotopic composition of seawater on geologic timescales. In particular, these systems represent an important sink of seawater Ca to the mantle and source of mantle Ca to seawater. It has been hypothesized that variations in the rate of seafloor spreading and associated fluxes of seawater through high temperature mid-ocean ridge (MOR) hydrothermal systems have produced large changes in the major element chemistry of seawater (Hardie, 1996; Holland, 2005). A better understanding of the chemical and isotopic fluxes of Ca through axial vent systems has important ramifications for understanding Ca cycling in modern and ancient oceans (De La Rocha and DePaolo, 2000; Fantle, 2010; Antonelli et al., 2017).

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As seawater is heated in the recharge zone of axial vent systems, anhydrite ($CaSO_4$) precipitation occurs at temperatures exceeding 140 °C (Bischoff and Seyfried, 1978). During discharge of fluids on and near the seafloor at deep sea vents, mixing of SO_4 rich seawater and Ca rich hydrothermal fluid also causes anhydrite to precipitate (Tivey et al., 1995). There is also evidence from drill cores, sulfur isotope analysis and theoretical calculations that anhydrite exists near the base of hydrothermal circulation cells (Ono et al., 2007; Alt et al., 2010; McDermott, 2015). Given its widespread occurrence in marine hydrothermal systems, anhydrite is thought to have significant effects on both the hydrogeology of the ocean crust, through porosity reduction during precipitation (Sleep, 1991; Lowell et al., 2003), and redox chemistry of high-temperature vent fluids (Seyfried and Ding, 1995).

In addition to fluid-rock interactions, phase separation of hydrothermal fluid influences the chemical and isotopic flux of dissolved components to the seafloor (Von Damm, 1995, 2004). Elemental partitioning and isotopic fractionation at pressure-temperature conditions representative of natural hydrothermal systems have been previously studied experimentally for a range of transition metals, alkali and alkali earth elements (Berndt et al., 1996; Heinrich et al., 1999; Liebscher et al., 2005, 2006; Foustoukos and Seyfried, 2007b; Rempel et al., 2012; Pokrovski et al., 2013; Syverson et al., 2014; Pester et al., 2015). These studies provide the solubility and isotopic constraints necessary to interpret field data taken from two-phase submarine (Foustoukos et al., 2004; Rouxel et al., 2004, 2008) and subaerial (Simmons and Brown, 2006; Hardardóttir et al., 2009) hydrothermal systems, while also serving as independent checks on first principle calculations of isotopic fractionation (Anbar et al., 2005; Chialvo and Horita, 2009; Rustad et al., 2010). Additionally, isotopic studies of two-phase fluid systems are useful to identify changes in aqueous speciation between vapor and liquid, given that, for many elements, the bonding and coordination environment in either phase often prefers one isotope relative to others (Liebscher et al., 2005, 2006; Rempel et al., 2012; Syverson et al., 2014). For example, Syverson et al. (2014) proposed that Fe isotope fractionation was caused by two distinct Fe species, $[FeCl_2(H_2O)_2]^0$ and $[FeCl_4]^{2-}$, coexisting in the vapor and liquid, respectively. With increasing departure from the two-phase boundary of the NaCl-H_2O system, the magnitude of Fe isotope fractionation increased as the two species presumably became more abundant in their respective phases.

In this study we present results from laboratory experiments of the $CaSO_4$-NaCl-H_2O system and natural samples from modern seafloor hydrothermal systems to determine: (1) the extent to which Ca isotopes fractionate during phase separation; (2) rates of anhydrite recrystallization as a function of dissolved Ca concentration; and, (3) the Ca isotopic composition of mid-ocean ridge hydrothermal fluids from two basalt-hosted vent systems. These data provide further constraints on the reactions responsible for Ca cycling within modern seafloor hydrothermal systems and a foundation for exploring how these systems may have changed over Earth history.

2. METHODS

2.1. Phase separation experiments

Phase separation experiments (experiments 1 and 2) were conducted at 420 and 450 °C between 31.0 and 46.0 MPa in flexible gold reaction cells (Seyfried et al., 1987). These temperatures and pressures were chosen in order to study Ca isotopic behavior at conditions representative of fast-spreading ridges at steady-state hydrothermal conditions (Foustoukos and Seyfried, 2007a; Fontaine et al., 2009; Pester et al., 2011, 2014). The NaCl composition of the two fluids at these conditions are well known (Sourirajan and Kennedy, 1962; Bischoff and Pitzer, 1989; Driesner, 2007; Driesner and Heinrich, 2007), and thus serve as a check for the results of the experiments presented here.

Experiments were performed isothermally and single-phase fluid samples were taken before decompressing to pressures within the vapor-liquid region. A Teledyne ISCO syringe pump remained connected to the pressurizing fluid that surrounds the gold reaction cell to control pressure within ±0.5 MPa of the reported value (see Fig. 1 in Berndt et al., 1996). For these experiments, the reaction time at a specific pressure-temperature condition ranged between 12 and 72.25 h, with the majority falling between 18 and 28 h. The sampling rate, manually controlled by a titanium-regulating valve, was maintained sufficiently low (<1 mL/min) so as to maintain steady-state conditions. As a result, neither temperature nor pressure changed by more than 1 °C or 0.1 MPa during sampling.

Given the volume limits of the gold reaction cell, care was taken to maintain the total volume of the system (vapor + liquid) below the maximum volume of the cell, $72\ cm^3$. The volume and mass fraction of each phase was calculated by mass balance on the bulk mole fraction of NaCl in the system. The NaCl composition of the two phases and the densities were taken from the literature (Driesner, 2007; Driesner and Heinrich, 2007).

Vapor and liquid samples were taken intermittently during experiment 1. Only samples of vapor were taken during the first decompression in experiment 2. The pressure was then increased to near the two-phase boundary and additional stock solution (Table 1) was added to the gold reaction cell with a second Teledyne ISCO syringe pump. The gold reaction cell and supporting pressure vessel were then rotated to allow for sampling of the liquid phase during a second stage of decompression.

All stock solutions (phase separation and isotope exchange experiments) were prepared with reagent grade salts and 18.2 mΩ deionized water. Samples were taken in clean pre-weighed luer lock syringes, weighed approximately 2 g and were separated into aliquots for total dissolved chemistry, Ca isotope and pH measurements. Before each sample, 0.3 g of fluid were removed and discarded to ensure that the fluid sample comes directly from the gold cell and not residual fluid in the capillary exit line. At the end of each experiment, 0.45 μm pore size nylon filters were used to filter anhydrite from solution and were dried for 24 h at 60 °C.