



# Experimental partitioning of Ca isotopes and Sr into anhydrite: Consequences for the cycling of Ca and Sr in subseafloor mid-ocean ridge hydrothermal systems

Drew D. Syverson<sup>a,b,c,\*</sup>, Peter Scheuermann<sup>b</sup>, John A. Higgins<sup>d</sup>, Nicholas J. Pester<sup>e</sup>, William E. Seyfried Jr.<sup>b</sup>

<sup>a</sup> Yale University, Department of Geology and Geophysics, 210 Whitney Ave., New Haven, CT 06511, USA

<sup>b</sup> University of Minnesota, Department of Earth Sciences, 310 Pillsbury Drive SE, Minneapolis, MN 55455-0231, USA

<sup>c</sup> Monash University, Department of Earth, Atmosphere and Environment, 9 Rainforest Walk, Building 28, Clayton, VIC 3800, Australia

<sup>d</sup> Princeton University, Department of Geosciences, Guyot Hall, Princeton, NJ 08544, USA

<sup>e</sup> Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, USA

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## Abstract

The elemental and isotopic mass balance of Ca and Sr between seawater and the oceanic crust at mid-ocean ridge (MOR) hydrothermal systems integrates various physiochemical processes in the subseafloor, such as dissolution of primary silicate minerals, formation of secondary minerals, and phase separation in the subseafloor. In particular, the precipitation and recrystallization of anhydrite are recognized as important processes controlling the Ca and Sr elemental and isotope composition of high temperature vent fluids and coexisting ocean crust, and yet, little experimental data exist to constrain the mechanism and magnitude of these critical geochemical effects. Thus, this study experimentally examines Sr/Ca partitioning, Ca isotope fractionation, and the rate of exchange between anhydrite and dissolved constituents. These experimental constraints are then compared with Sr/Ca and Ca isotope compositions of anhydrite and vent fluids sampled from the TAG hydrothermal system. Accordingly, anhydrite precipitation and recrystallization experiments were performed at 175, 250, and 350 °C and 500 bar at chemical conditions characteristic of active MOR hydrothermal systems. Experimental data suggest that upon entrainment and recharge of seawater into MOR hydrothermal systems anhydrite will rapidly precipitate with a Ca isotopic composition that is depleted in the heavy isotope compared to the hydrothermal fluid. The magnitude of the Ca isotope fractionation,  $\Delta^{44/40}\text{Ca}_{(\text{Anh-Fluid})}$ , is temperature dependent,  $-0.45$ ,  $-0.22$ , and  $-0.02\%$ , for 175, 250, and 350 °C, respectively, but likely indicative of kinetic effects. Utilization of a  $^{43}\text{Ca}$  spike in solution was implemented to quantify the time-dependent extent of isotope exchange during anhydrite recrystallization at chemical equilibrium. These data indicate that the rate of exchange is a function of temperature, where 12, 46, and 45% exchange occurred within 1322, 867, 366 h at 175, 250, and 350 °C, respectively. The partitioning of Sr/Ca between anhydrite and constituent dissolved species during precipitation depends greatly on the saturation state of the hydrothermal fluid with respect to anhydrite at each experimental temperature,  $K_{\text{D}(\text{Anh-Fluid})} = 1.24\text{--}0.55$  at 175–350 °C, broadly similar to results of earlier experimental observations by Shikazono and Holland (1983). Equilibrium  $K_{\text{D}(\text{Anh-Fluid})}$  values were estimated by taking explicit account of time dependent magnitude of exchange, yielding values of 0.43, 0.36, 0.29 at 175, 250, and 350 °C, respectively. Coupling these experimental constraints with the temperature gradient inferred for high temperature MOR hydrothermal systems suggests that the Ca isotope and Sr elemental composition of anhydrite formed near the seafloor will retain the composition derived upon initial formation conditions, which is indicative of disequilibrium. In contrast, at greater depths and at higher temperatures, anhydrite will reflect

\* Corresponding author at: Yale University, Department of Geology and Geophysics, 210 Whitney Ave., New Haven, CT 06511, USA.  
E-mail address: [drew.syverson@yale.edu](mailto:drew.syverson@yale.edu) (D.D. Syverson).

close to equilibrium Sr/Ca partitioning and Ca isotope fractionation conditions. The experimental and natural data presented in this study can be used to further understand the effect of anhydrite precipitation during hydrothermal circulation in the oceanic crust and on the chemical and isotopic composition of seawater on geologic timescales.

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## 1. INTRODUCTION

The formation of anhydrite ( $\text{CaSO}_4$ ) in active high temperature mid-ocean ridge (MOR) hydrothermal systems occurs as a consequence of conductive heating of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ -bearing seawater that is recharged into the oceanic crust and during mixing of high temperature hydrothermal fluid with seawater at vent sites on the seafloor (Fig. 1). This reaction is thought to be widespread in modern oceanic mid-ocean ridge hydrothermal systems due to the inherent retrograde solubility of anhydrite at pressure, temperature, and chemical conditions indicative of MOR hydrothermal systems and the high  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  contents of modern seawater (Bischoff and Seyfried, 1978; Seyfried and Ding, 1993; Newton and Manning, 2004). However, in spite of the ubiquitous occurrence of anhydrite in high temperature MOR hydrothermal systems, very little anhydrite is preserved in older oceanic crust and the importance of subseafloor anhydrite as a long-term sink of seawater  $\text{SO}_4^{2-}$  and/or  $\text{Ca}^{2+}$  is controversial (Sleep, 1991; Alt, 1995; Teagle et al., 1998b; Alt et al., 2003). In addition to MOR hydrothermal systems, anhydrite also persistently forms in oceanic back-arc basin hydrothermal systems and in continental hosted porphyry hydrothermal deposits as a consequence of heating and mixing of fluids that are concentrated in  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . Geologic environment notwithstanding, anhydrite formation has important geophysical and geochemical implications for fluid flow in the crust, elemental cycling between rock and fluid reservoirs, and hydrothermal processes such as redox buffering and mineral deposition associated with the formation of economic ore deposits (Lowell et al., 2003; Ono et al., 2007; Tolstoy et al., 2008; Craddock et al., 2010; Peters et al., 2010; Blundy et al., 2015; McDermott et al., 2015; Nadeau, 2015).

Geochemical tracers that have been applied to the study of anhydrite formation in subseafloor hydrothermal systems include Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios,  $^{18}\text{O}/^{16}\text{O}$  ratios, and multiple S isotope ratios ( $^{34}\text{S}/^{32}\text{S}$  and  $^{33}\text{S}/^{32}\text{S}$ ) (Chiba et al., 1998; Teagle et al., 1998a; Mills and Tivey, 1999; Ono et al., 2007; Peters et al., 2010). These applications benefit from experimental studies bearing on the redox and temperature dependent stability of anhydrite at elevated temperature and pressures (Ohmoto and Rye, 1979; Chiba et al., 1981; Ohmoto and Lasaga, 1982). In combination, these data have shown that seawater pervasively enters the subseafloor and mixes with high temperature hydrothermal fluids, inducing the formation of extensive sulfide deposits at and below the seafloor. In addition, these data have helped to constrain the degree of water-rock interaction in the subseafloor, while further documenting

microbial effects that influence mass transfer of elements between seawater and the oceanic crust. However, complementary elemental and isotopic systems, such as Ca, have not been studied extensively and may provide important additional information that can further elucidate the temporal and spatial evolution of marine hydrothermal systems.

Previous experimental efforts precipitated anhydrite upon heating Ca and  $\text{SO}_4$  bearing fluid, although equilibrium phase relations were not determined unambiguously (Shikazono and Holland, 1983). The experimental data reported here not only address anhydrite solubility, but also quantify the magnitude and sign of fractionation of Ca isotopes during anhydrite precipitation. These data benefit from careful analysis of the effect of temperature and time on the rate of exchange of Ca isotopes between anhydrite and dissolved  $\text{Ca}^{2+}$  species, with implications for interpretation of the physiochemical characteristics of active MOR and oceanic/continental volcanic arc hydrothermal systems, especially since anhydrite precipitation has been invoked as an important process in the Ca isotope budget of subseafloor hydrothermal systems but comparable experimental data are lacking (Amini et al., 2008).

With the continued advancement of multi-collector ICP-MS (MC-ICP-MS) technology and increasingly more sophisticated techniques and procedures for isotopic analysis and experimentation, the Ca isotope composition of hydrothermal fluids and coexisting minerals from MOR systems are now being determined to better understand subseafloor hydrothermal processes. However, there are few experimental data with respect to the Ca isotope system to broaden the interpretation of fluid and mineral alteration processes in natural hydrothermal systems. Furthermore, Ca isotopes can be used to trace rates and mechanisms of mass transfer in experimental studies, with important implications for testing equilibrium Sr/Ca partitioning,  $K_D$ , between anhydrite and fluid, despite incomplete exchange between distinct chemical reservoirs.

This study examines two important geochemical tracers, Ca isotope fractionation and partitioning of elemental Sr, during precipitation and recrystallization of anhydrite at 175, 250, and 350 °C and 500 bars at controlled chemical conditions in hydrothermal experiments. Experimental constraints are then compared with Ca and Sr elemental and isotopic compositions of hydrothermal fluid – anhydrite pairs recovered from the MOR hydrothermal systems, Logatchev and TAG, as presented by Amini et al. (2008) and this study, respectively. In addition, the experimental and natural data presented in this study are also compared with a limited number of measured end-member hydrothermal fluids from a variety of MOR hydrothermal systems

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