RESEARCH ARTICLE
10.1029/2022GC010471

Key Points:
- Mg isotopes in fluids from Macauley imply Mg enrichment by phase separation
- Mg isotopes in fluids from Brothers indicate leaching of Mg from the basement
- $^{26}$Mg is preferentially incorporated into caminite

Supporting Information:
Supporting Information may be found in the online version of this article.

Correspondence to:
F. K. Wilckens, fwilckens@marum.de

Author Contributions:
Conceptualization: Frederike K. Wilckens, Christian T. Hansen, Wolfgang Bach, Simone A. Kasemann
Funding acquisition: Wolfgang Bach, Simone A. Kasemann
Methodology: Frederike K. Wilckens, Christian T. Hansen, Alexander Diehl
Project Administration: Wolfgang Bach, Simone A. Kasemann
Supervision: Wolfgang Bach, Simone A. Kasemann
Validation: Wolfgang Bach
Writing – original draft: Frederike K. Wilckens
Writing – review & editing: Christian T. Hansen, Alexander Diehl, Wolfgang Bach, Simone A. Kasemann

© 2022. The Authors. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Sources of Mg Enrichments in Vent Fluids From the Kermadec Arc Recorded by Li, B, and Mg Isotopes

Frederike K. Wilckens$^1$, Christian T. Hansen$^1$, Alexander Diehl$^1$, Wolfgang Bach$^1$, and Simone A. Kasemann$^1$

$^1$MARUM – Center for Marine Environmental Sciences and Faculty of Geosciences, University of Bremen, Bremen, Germany

Abstract Magnesium concentrations in acid-sulfate fluids from Brothers and Macauley volcano, Kermadec arc, Western Pacific, exceed those of seawater and differ from previously known acid-sulfate fluids with seawater-like Mg concentrations. Earlier studies explained these Mg enrichments as due to phase separation, caminite ($\text{Mg}_{1.25}\text{SO}_4(\text{OH})_0.5 \times 0.5\text{H}_2\text{O}$) dissolution, water-rock interaction and/or "mining" of deep seated magmatic brines. Since these different and partly contradictory explanations could neither be confirmed nor refuted, we investigated B, Li, and Mg isotope compositions in acid-sulfate and black smoker fluids from both Brothers and Macauley to understand the origin of the high Mg concentrations and investigate a possible connection with the alteration of basement rocks. In addition, we performed seawater heating experiments to investigate Mg isotope fractionation during caminite precipitation. Lithium and B isotope signatures in all studied acid-sulfate fluids indicate water-rock interaction. Magnesium isotopes in fluids from Macauley correspond to seawater, implying Mg enrichment through phase separation in the fluids. In contrast, Mg-enriched acid-sulfate fluids from Brothers volcano have higher $\delta^{26}$Mg values (up to $-0.62\%$) than seawater. Considering that our seawater heating experiment shows a preferential incorporation of $^{24}$Mg into caminite, caminite dissolution would lead to lower $\delta^{26}$Mg values and thus cannot solely account for the enriched Mg concentrations seen at Brothers. Additionally, we thus suppose leaching of Mg from the basement during the interaction of acidic fluids with a relatively unaltered basement.

1. Introduction

Hydrothermal circulation, in particular high-temperature interaction between seawater and oceanic crust, is one of the main sinks for magnesium (Mg) in seawater (Elderfield & Schulz, 1996). During this interaction, Mg is incorporated into secondary minerals. As a result, high-temperature (300°C–400°C) black-smoker hydrothermal vent fluids have Mg contents close to zero (i.e., von Damm et al., 1985). Experimental studies and natural observations suggest that Mg removal is almost complete during water-rock interaction at elevated (>60°C) temperatures (i.e., Mottl & Wheat, 1994; Seyfried & Bischoff, 1979; Seyfried & Mottl, 1982). However, vent fluids with Mg concentrations similar to seawater were found in numerous arc and backarc hydrothermal systems, although the fluids were clearly hot enough (90°C–215°C) to expect strong Mg-depletions (i.e., Butterfield et al., 2011; de Ronde et al., 2011; Gamo et al., 1997; Seewald et al., 2015, 2019). Since these fluids are also characterized by high acidity and high sulfate concentrations, they are commonly known as acid-sulfate fluids. Besides these diverging chemical characteristics (i.e., low pH, high $\text{SO}_4^{2-}$, and high Mg), acid-sulfate fluids are also not as hot (<215°C) as their black-smoker type counterparts (>300°C). Hence, it was suggested that the acid-sulfate fluids form by a mechanism different from the high-temperature water-rock reactions that give rise to the formation of black smoker fluids (low $\text{SO}_4^{2-}$ and Mg) (de Ronde et al., 2011; Gamo et al., 1997; Seewald et al., 2015; Stucker et al., 2017). In the suggested model, degassing of a magmatic vapor phase released from an underlying magma reservoir plays a key role, and these vapors heat seawater in the shallow volcanic basement to generate the acid-sulfate fluids (Butterfield et al., 2011; de Ronde et al., 2005, 2011; Gamo et al., 1997; Seewald et al., 2015). This idea that seawater in the acid-sulfate vents is heated by influxing magmatic vapor helps to explain the seawater-like Mg concentrations in acid-sulfate fluids, because seawater does not react as much with the basement as in a system where the heat is mined from hot rock (Seewald et al., 2015, 2019). This hypothesis has been supported by the seawater-like Mg isotope compositions of acid-sulfate fluids (Wilckens et al., 2019), suggesting that Mg had apparently not taken part in these reactions.
Recent studies (Kleint et al., 2019; Stucker et al., 2022) reported acid-sulfate fluids from the Kermadec arc (Figure 1) that have significant Mg enrichments (up to 95.6 mM) compared to seawater (53.1 mM). These fluids are from the Macauley (Figure 2a) hydrothermal vent site and the Lower Cone hydrothermal site at Brothers volcano (Figure 2b). The fluids from Macauley are acidic (pH of 2) and have high Cl concentrations of up to 787 mM. Chlorine shows positive correlations with Mg and most other elements and can hence not be attributed to an influx of HCl related to degassing. Kleint et al. (2019) hence explained the geochemical signature of the fluids by phase separation (venting of the brine phase) and water-rock interaction. The unusual Mg enrichment has been explained by a combination of very acidic fluids interacting with a relatively young volcanic basement or by low fluid discharge. By contrast, the fluids venting at the Lower Cone of Brothers volcano have seawater-like Cl concentrations, higher pH values (between 3.8 and 4.8), high \( \text{SO}_4^{2-} \) concentrations (up to 76.9 mM), yet the highest Mg concentrations (up to 95.6 mM) measured in acid-sulfate fluids to date. Kleint et al. (2019) explained the high Mg and \( \text{SO}_4^{2-} \) concentrations in the Lower Cone fluids via dissolution of caminite, a magnesium hydroxide sulfate hydrate (MHS) mineral, often proposed to have the composition \( \text{Mg}_7(\text{SO}_4)_5(\text{OH})_4 \times 2 \text{H}_2\text{O} \), found in the wall of a black-smoker chimney on the East Pacific Rise (Haymon & Kastner, 1981). It has been demonstrated that MHS phases form when seawater is heated to temperatures above 250°C, but they dissolve rapidly in seawater at lower temperatures (Bischoff & Seyfried, 1978; Janecky & Seyfried, 1983). At 350°C this phase has the composition \( \text{Mg}_{1.25}\text{SO}_4(\text{OH})_{0.5} \times 0.5\text{H}_2\text{O} \) and thermodynamic data for it exists that allow examination of its stability (Janecky & Seyfried, 1983). As expected from the phase relations, there is no evidence of caminite in drill cores from Brothers Cone (de Ronde, Humphris, & Höfig, 2019). Peters et al. (2021) later therefore proposed that the fluids at Brothers Cones are affected by the dissolution of natroalunite and by \( \text{SO}_2 \) disproportionation. This process can explain the elevated sulfate concentrations in the Cone fluids but not the high Mg concentrations. Finally, Stucker et al. (2022) suggested that the higher-than-seawater values for Mg in the Lower Cone fluids cannot be explained by phase separation or dissolution of caminite, but may instead be due to the dissolution of deep seated hypersaline brines (32–45 wt. % NaCl equiv.; de Ronde, Humphris, Höfig, et al., 2019). Since none of the above hypotheses have been soundly refuted or confirmed, we are trying to solve the Mg conundrum using a different approach—Mg isotopes.
The magnesium isotope composition in hydrothermal fluids can be influenced by several processes within the ocean crust (Figure 3a). The main source of Mg in hydrothermal fluids is seawater, which has a uniform Mg concentration of about 53 mM and a Mg isotope composition of δ^{26}Mg = −0.82‰ ± 0.06‰ (Foster et al., 2010; Figure 3a). Recent studies show a significant Mg isotope fractionation during high-temperature interaction between seawater and the ocean crust, with the heavier ^{26}Mg isotope preferentially incorporated into secondary minerals (Eom et al., 2020; Voigt et al., 2020). Other processes that may affect the Mg isotope composition of vent fluids are phase separation and segregation, but recent results imply that it is negligible (Eom et al., 2020). By contrast, dissolution of Mg-bearing minerals could affect the Mg isotope composition. That is, mid-ocean ridge basalts and island arc basalts have a different Mg isotope composition than seawater, with δ^{26}Mg values of about −0.26‰ ± 0.07‰ (2SD, n = 110; Teng et al., 2010). Hydrothermally altered ocean crust and island arc lavas have similar, or higher δ^{26}Mg values (−0.25‰ to 0‰ and −0.25‰ to −0.1‰, respectively; J. Huang et al., 2015, K.-J. Huang et al., 2018; Teng et al., 2016). Therefore, Mg leached from the basement rocks could lead to higher δ^{26}Mg values in the fluid (Figure 3a). Further, Schmidt et al. (2019) explained the high δ^{26}Mg values they detected in pore fluids from the Terceira Rift, Azores, with the dissolution of caminite.

To trace water-rock interactions and especially the origin of the Mg, we performed B, Li and Mg isotope analyses in the fluids from Macauley and Brothers volcano sites. In addition, we performed an experiment in which we heated seawater to 350°C and investigated the Mg partitioning and isotope fractionation during caminite precipitation; these results were then used to explain the data observed in the sampled vent fluids.

2. Study Area

The intra-oceanic Kermadec arc is located in the Western Pacific northeast of New Zealand and is part of the Kermadec-Tonga arc formed by the subduction of the Pacific plate underneath the Australian plate (Figure 1). The convergence rate is 4 cm/a in the south and 8 cm/a in the north (DeMets et al., 1994, 2010). Volcanism in the southernmost part of the Kermadec arc is believed to be influenced by a flux of sediment and slab-derived volatiles in the form of the subduction of the Hikurangi Plateau (Timm et al., 2014). The Kermadec arc is a very hydrothermally active arc on a world scale (de Ronde et al., 2003), and hosts about 34 large volcanic structures with at least 19 active vent sites, including those at Macauley and Brothers volcano (de Ronde et al., 2007).

2.1. Macauley

Macauley volcano is located in the central part of the Kermadec arc (Figure 1). Its caldera has a diameter of about 10 km (Wright et al., 2006). The volcanic rocks of Macauley Volcano cover a wide range of composition with dacitic to rhyolitic as well as basaltic compositions (Barker et al., 2013; Wright et al., 2006). The most obvious hydrothermal activity within the volcano is located inside the crater rim of a >500-m tall emergent cone in the
southeastern section of the caldera (Figure 2a). Here, vent fluids discharge at a depth of 336 m on the southeastern inner wall of the crater rim and are associated with precipitation of native sulfur. The fluids have been characterized as acid-sulfate fluids with a maximum venting temperature of 110°C and a low pH of <1.5 (Kleint et al., 2019).

2.2. Brothers Volcano

Brothers volcano is located approximately 600 km southwest of Macauley caldera in the southern part of the Kermadec arc and is potentially influenced by the subduction of the Hikurangi Plateau (de Ronde et al., 2007; Figure 1). The oval-shaped caldera covers 3 km × 4 km and its floor reaches 1,850 mbsl at its deepest point. The caldera rim shoals to 1,540 mbsl (de Ronde, Humphris, Höfig, et al., 2019; de Ronde et al., 2005). It is considered the most hydrothermally active volcano in the Kermadec arc (de Ronde et al., 2001) and has five sites of active fluid discharge (Baker et al., 2012; de Ronde et al., 2011). High-temperature black smoker fluids (<320°C) with moderate pH values (i.e., between 3.1 and 3.5) are venting from several vent fields along the caldera walls (i.e., NW Caldera, Upper Caldera, and W Caldera sites), while acid-sulfate fluids are venting at the summit areas of two post caldera cones that rise 500–800 m above the caldera floor: Upper Cone (T = 122°C and pH of 1.9) and Lower Cone (T < 83°C and pH > 3.8) (Figure 2b) (de Ronde et al., 2005, 2011; Kleint et al., 2019; Stucker et al., 2022). The volcanic rocks recovered from the caldera range from dacitic to rhyolitic compositions with high alkali concentrations (Berkenbosch et al., 2012, 2015; Haase et al., 2006; Wright & Gamble, 1999). Hydrothermal alteration at the different venting sites (i.e., high temperature vs. acid-sulfate fluids) varies widely with secondary mineral assemblages comprising chlorite, illite, quartz and pyrite occurring at and just below the seafloor at the NW Caldera site, with advanced argillic alteration assemblages containing pyrophyllite, natroalunite, native sulfur, and quartz seen at the Cone sites. A similar advanced argillic alteration assemblage (with diaspore) was found to lie beneath the chlorite-rich assemblage at the NW Caldera sites (de Ronde, Humphris, & Höfig, 2019, de Ronde, Humphris, Höfig, et al., 2019).

3. Methods

3.1. Sample Collection of Hydrothermal Fluids

All vent fluid samples were collected during SO253 expedition aboard R/V Sonne between December 2016 and January 2017 using the remotely operated vehicle (ROV) MARUM-QUEST 4000 (Table 1). Sampling of hydrothermal fluids was done with isobaric gas-tight (IGT) fluid samplers and titanium syringe style “Major” samplers deployed on the ROV. Real-time measurements of temperature were acquired during IGT sampling. For isotope analyses, the vent fluid samples were filtered on-board using 0.2 μm Nuclepore polycarbonate membrane filters and stored in 5 ml Zinsser vials. The physical parameters and chemical composition of the fluids from Macauley and Brothers caldera have been described and discussed in Kleint et al. (2019).

3.2. Sample Preparation and Isotope Analyses

Fifteen samples from Brothers volcano and three samples from Macauley caldera were selected for the analysis of B, Li, and Mg isotopes. Isotope ratios were measured on a ThermoFisher Scientific Neptune Plus Multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) located at the Isotope Geochemistry Laboratory at MARUM—Centre for Marine Environmental Sciences, University of Bremen. For the isotope measurements, the MC-ICP-MS was equipped with a stable introduction system, a standard sample cone and a high efficiency x-cone. Prior to the isotope measurements, B, Li, and Mg were separated from the sample matrix using specific separation methods (see below).

3.2.1. Boron Isotope Ratios

Boron was separated from the sample matrix using the micro sublimation method described in Hüpers et al. (2016). Approximately 300 ng of B was used for every sublimation and mixed with ultrapure water in the lid of a 5 ml conical Savillex beaker in order to have matching sample volumes (45 μl) for all samples. Subsequently, 5 μl 7N HNO₃ was added to this mixture and the beakers were sealed with a cover of aluminum foil and reacted for at least 18 hr at 98°C.
For B isotope analyses, purified samples, processed reference materials, and the internal laboratory standard were diluted with 2% HNO₃ to a concentration of 100 ng/g B. Intensity matching between samples and standard was better than 10%. Boron isotope measurements were done with the standard-sample-bracketing method in low resolution with NIST SRM951 as the bracketing standard. The B isotope ratios are reported in the conventional δ-notation (‰) and were normalized to the reference material NIST SRM 951. To control the quality of the preparation and isotope measurements, an internal laboratory seawater standard (bottom seawater from SuSu Knolls) has been analyzed and gives a δ¹¹B value of +39.73 ± 0.18 (2SD, n = 3), which agrees with published δ¹¹B values for seawater (i.e., +39.61 ± 0.2; 2SD mean, n = 28; Foster et al., 2010). The precision is better than 0.3‰ (2SD), which is based on repeatedly prepared and analyzed reference materials during the period of the measurements. The long-term repeatability of the NIST SRM 951 is +0.04‰ ± 0.17‰ (2SD, n = 4). Based on a minimum of three isotope measurements, the uncertainty of the samples is reported as 2SD.

3.2.2. Lithium Isotope Ratios

Approximately 100 ng of Li was separated from matrix elements using a two-step cation chromatographic separation modified after Moriguti and Nakamura (1998), and described in detail in Hansen et al. (2017). Every sample batch contained two reference materials (to verify the accuracy and precision of the analytical procedure) and a procedural blank. To avoid matrix effects during isotope analyses, the purified Li fractions were checked for impurities of matrix elements. Further, to evaluate Li loss during the separation procedure, cuts before and after Li elution were screened for Li with yields >99.7%. Procedural blanks are lower than 0.01%.

Lithium isotope analyses were also performed using the standard-sample bracketing method in low resolution and the international reference material NIST RM 8545 (L-SVEC) as the bracketing standard. Lithium concentrations

| Area                  | Sample ID         | Depth | T_max a (°C) | pH a | B a (μM) | Li a (μM) | Mg a (mM) | δ¹¹B ± 2SD | δ⁷Li ± 2SD | δ²⁶Mg ± 2SD |
|-----------------------|-------------------|-------|--------------|------|----------|-----------|-----------|------------|------------|-------------|
| Seawater              |                   |       |              |      |          |           |           |            |            |             |
| Macauley              | SO253_009_ROV_2F  | 336   | 7.8          | 400  | 27.3     | 53.1      | 39.7 ± 0.2| 30.9 ± 0.2| -0.87 ± 0.07|
|                       | SO253_013_ROV_2F  | 336   | 1.5          | 594  | 102      | 66.8      | 27.3 ± 0.1| 12.4 ± 0.1| -0.89 ± 0.08|
|                       | SO253_013_ROV_3F  | 336   | 1.2          | 609  | 94       | 68.9      | 27.2 ± 0.0| 12.2 ± 0.0| -0.89 ± 0.03|
| Brothers lower cone   | SO253_045_ROV_3F  | 1,318 | 67           | 4.8  | 429      | 56        | 82.6      | 36.1 ± 0.1| 14.5 ± 0.1| -0.71 ± 0.02|
|                       | SO253_045_ROV_4F  | 1,318 | 67           | 4.4  | 419      | 56        | 79.0      | 36.1 ± 0.1| 14.1 ± 0.2| -0.67 ± 0.04|
|                       | SO253_045_ROV_5F  | 1,318 | 70           | 4.5  | 418      | 57        | 79.0      | 36.0 ± 0.1| n.d.       | n.d.        |
|                       | SO253_045_ROV_9F/10F | 1,332 | 78           | 4.5  | 402      | 44        | 75.4      | 37.5 ± 0.2| 18.5 ± 0.3| -0.71 ± 0.04|
|                       | SO253_045_ROV_11F | 1,331 | 83           | 3.8  | 428      | 60        | 95.6      | 35.1 ± 0.1| 14.0 ± 0.1| -0.62 ± 0.04|
| Brothers upper cone   | SO253_048_ROV_2F  | 1,217 | 115          | 2.4  | 415      | 45        | 52.7      | 35.7 ± 0.0| 18.0 ± 0.3| n.d.        |
|                       | SO253_048_ROV_10F | 1,218 | 83           | 2.1  | 458      | 65        | 55.3      | 32.9 ± 0.1| n.d.       | -0.90 ± 0.05|
| NW caldera            | SO253_061_ROV_2F  | 1,670 | 248          | 3.9  | 839      | 399       | 26.8      | 21.3 ± 0.0| n.d.       | n.d.        |
|                       | SO253_061_ROV_3F  | 1,670 | 248          | 3.4  | 889      | 509       | 21.8      | 20.1 ± 0.1| 5.9 ± 0.2 | -0.87 ± 0.05|
|                       | SO253_064_ROV_4F  | 1,590 | 264          | 4.4  | 1,240    | 744       | 10.2      | 18.5 ± 0.1| n.d.       | n.d.        |
|                       | SO253_064_ROV_5F  | 1,600 | 264          | 3.5  | 1,270    | 790       | 4.3       | 17.7 ± 0.2| 5.4 ± 0.1 | -0.91 ± 0.04|
| NW caldera            | SO253_072_ROV_4F  | 1,617 | 223          | 3.1  | 889      | 526       | 18.2      | 21.0 ± 0.2| 5.7 ± 0.2  | n.d.        |
|                       | SO253_072_ROV_5F  | 1,617 | 223          | 3.1  | 981      | 563       | 18.1      | 21.0 ± 0.0| n.d.       | n.d.        |
| NW caldera            | SO253_081_ROV_2F  | 1,619 | 304-305      | 3.3  | 1,330    | 815       | 3.2       | 17.6 ± 0.1| 5.4 ± 0.1 | n.d.        |
|                       | SO253_067_ROV_10F | 1,374 | 310–311      | 3.2  | 1,160    | 754       | 5.4       | 18.2 ± 0.1| 4.7 ± 0.1 | n.d.        |
|                       | SO253_067_ROV_12F | 1,374 | 310–311      | 3.1  | 1,110    | 687       | 4.9       | 18.3 ± 0.0| n.d.       | n.d.        |

Note. mM, mmol/kg; μM, μmol/kg; n.d. = not determined, T_max = maximum temperature.

aPreviously reported by Kleint et al. (2019).
of the samples and reference materials were diluted with 2% HNO₃ to 25 ng/g. Lithium isotope ratios are normalized to L-SVEC and reported in the conventional δ-notation (‰). Fully processed NIST RM 8545 gives a δ⁷Li value of 0.0‰ ± 0.1‰ (2SD, n = 4), and the internal seawater standard (bottom seawater from Susu Knolls) gives a δ⁷Li values of +30.9‰ ± 0.2‰ (2SD, n = 2), which agrees with published values for IAPSO seawater reference material (i.e., +31.2‰ ± 0.9‰ (2SDmean, n = 44; Pogge von Strandmann et al., 2010)). The uncertainty of the samples is reported as 2SD based on at least three individual isotope measurements.

3.2.3. Magnesium Isotope Ratios

To separate Mg from the matrix elements we used a one-step cation chromatographic column separation as described in Dämmer et al. (2021). One to 2 μg of Mg were loaded onto the columns and separated from the sample matrix. Every sample batch contained two reference materials (to verify the accuracy and precision of the analytical procedure) and a procedural blank. To avoid matrix effects during isotope analyses, the purified Mg fractions were checked for impurities of matrix elements. To evaluate Mg loss during the separation procedure, cuts before and after Mg elution were screened for Mg. Procedural blanks are lower than 1 ng Mg.

For Mg isotope measurements, samples and standards were diluted to 100 ng/g Mg solutions in 2% HNO₃ and analyzed using the standard-sample bracketing method in low resolution with an ICP Mg standard (Alfa Aesar Magnesium plasma standard solution, Specpure) as the bracketing standard. Magnesium isotope ratios are reported in the conventional δ-notation (δ²⁶Mg and δ²⁵Mg). For the conversion of δ²⁶Mg and δ²⁵Mg to the DSM-3 scale and to evaluate single measurement sequences, the international reference materials DSM-3 and Cambridge-1 (Cam-1) were analyzed in every sequence. The repeatability for δ²⁶Mg values was ±0.06‰ (2SD, n = 6) based on repeated analyses of Cam-1 during the period of the measurements. Repeated analyses of an internal laboratory seawater standard (bottom seawater from SuSu Knolls) gave a δ²⁶Mg value of −0.87‰ ± 0.07‰ (2SD, n = 7), which agrees with published values for seawater (i.e., δ²⁶Mg = −0.82‰ ± 0.06‰, 2SDmean, n = 43, Foster et al., 2010). The uncertainty of the samples is reported as 2SD based on at least three individual isotope measurements.

3.3. End-Member Calculation for Black Smoker Fluids

Vent fluids recovered from seafloor sites can be influenced by mixing with unmodified seawater during sampling and thus may represent two-component mixtures of hydrothermal fluids and seawater. Based on their low Mg concentrations, the high-temperature fluids from the caldera sites of Brothers volcano are thought to have a Mg concentration of Mg = 0 mM in the pure hydrothermal end-member (EM; see de Ronde et al., 2011; Kleint et al., 2019; Stucker et al., 2022). To calculate the pure hydrothermal EM for the individual orifices, we performed a linear extrapolation to zero-Mg using the measured Mg concentrations of the vent fluid samples and seawater as described in Von Damm et al. (1985). Only samples containing less than 10 mmol/kg Mg were considered for the EM calculation. There is no calculation of EM Mg isotope composition possible, as Mg is assumed to be zero in the pure hydrothermal vent fluid. Because Mg is not removed during formation of acid-sulfate fluids, EM compositions of acid-sulfate fluids could not be determined.

3.4. Experimental Setup

The effect on Mg isotope geochemistry during heating of seawater in hydrothermal systems was investigated using a customized Dickson-type reactor (cf. Dickson et al., 1963; Seyfried, 1987). Approximately 65 mL of a deep seawater sample collected by rosette bottles attached to a CTD (R/V Polarstern expedition PS101; 2,500 m water depth, salinity ≈36‰) were transferred into a flexible gold reaction cell (Vtotal ≈100 mL), which is connected to a titanium access tube with an in-line 2 μm Ti-filter. The sealed reaction cell is encased in a stainless-steel pressure vessel (Parr Instruments) filled with distilled water and the entire vessel is placed in an electric ceramic heater arrangement allowing for independent control of temperature and pressure. All components in contact with the autoclaved seawater were made of either unreactive passivated titanium, or gold. The setup was heated to 350°C while maintaining a constant pressure around 40 MPa, similar to earlier experiments by Bischoff and Seyfried (1978) and Janecky and Seyfried (1983). During heating of the seawater, in-situ fluid samples were taken through the access tube to keep track of the evolving fluid composition. Fluid samples were collected 3, 16.5, 23.5, and 40.5 hr after start of the experiment. The experiment was terminated after 40 hr.
The collected fluid samples were analyzed for their pH, salinity, major element fluid chemistry, and Mg isotopic composition. Salinity was determined with an Atago® Master-S/Millα refractometer and used as an indicator of potential leakage between pressure vessel and reaction cell. Evolving pH was measured at 25°C using a micro-pH-combined A-157 electrode attached to a Schott® Instruments Lab 850 device following a three-point calibration with suitable Schott® buffer solutions (pH 4.01, 7.00, and 10.01). Dissolved elemental concentrations were determined via ICP OES (Agilent 720) and IC (IC Metrohm CompactIC) in the Sediment Geochemistry Group of MARUM, University of Bremen. Precision (Sr <3.2%, Ca <0.8%, SO4 <1.0%, and Mg <1.2%, 2 RSD) and accuracy (<10.5% for Sr and Ca, <14% for SO4, and <6% for Mg 1 SDmean) were established through replicated measurements of certified seawater reference material (NRCC NASS-5). Analytical uncertainty of pH measurements were ±0.05 pH units.

4. Results

4.1. Isotope Data of the Vent Fluids

The isotope composition of B, Li, and Mg for the vent fluids together with previously published concentration data, temperatures and pH (Kleint et al., 2019) are summarized in Table 1. Calculated EM compositions for the black smoker fluids from the Brothers NW Caldera site are summarized in Table 2.

4.1.1. Black Smoker Fluids

δ7Li and δ11B values in the black smoker fluids from the Brothers Caldera site are significantly lower than seawater ranging from +4.7‰ to +5.9‰ and 17.6‰–21.3‰, respectively. The calculated EM compositions of the black smoker fluids range between +4.6‰ and +5.3‰ for δ7Li and between 17.1 and 17.5 for δ11B.

4.1.2. Acid-Sulfate Fluids

δ11B values in the acid-sulfate fluids from Brothers volcano (Lower and Upper Cone) and Macauley are also lower than seawater, but higher than the black smoker fluids, with values ranging between 35.1‰ and 37.5‰, and between 27.2‰ and 27.7‰, respectively. δ7Li values for acid-sulfate fluids at Macauley are between 12.2‰ and 12.4‰, which are lower than those for the Brothers Cone sites, with values between 14.0‰ and 18.0‰.

Acid-sulfate fluids from Macauley and the Upper Cone site at Brothers volcano have δ26Mg values that match seawater, with values between −0.86‰ and −0.89‰ and −0.90‰, respectively. The acid-sulfate fluids from the Lower Cone have higher δ26Mg values, between −0.62‰ and −0.67‰ (Figure 3b).

4.2. Chemical Composition of Fluids During the Experiment

The chemical composition and Mg isotope ratios for the fluid samples analyzed during the experiment are summarized in Table 3. The starting seawater solution has an initial concentration of 10.2 mmol/l for Ca, 55.2 mmol/l for Mg and 29.8 mmol/l for SO42−. The fluid samples collected 3, 16.5, 23.5, and 40.5 hr after start of the experiment are all depleted in Ca, Mg, and SO42−, with Ca concentrations as low as 1.0 mmol/l, Mg between 40.7 and

| Sample ID       | Area               | B (μM) | Li (mM) | δ11B (‰) | δ7Li (‰) |
|-----------------|--------------------|--------|---------|-----------|----------|
| SO253_067_ROV_10F | Upper wall         | 1,247  | 856     | 17.4      | 4.6      |
| SO253_067_ROV_12F | Upper wall         | 1,183  | 820     | 17.5      | n.d.     |
| SO253_064_ROV_4F  | NW caldera wall    | 1,439  | 947     | 17.1      | n.d.     |
| SO253_064_ROV_5F  | NW caldera wall    | 1,347  | 878     | 17.1      | 5.3      |
| SO253_081_ROV_2F  | NW caldera wall    | 1,390  | 935     | 17.2      | 5.3      |

Note. mM, mmol/kg; μM, μmol/kg; n.d. = not determined.
42.3 mmol/l, and $\text{SO}_4^{2-}$ between 9.8 and 10.1 mmol/l. The pH dropped from 7.5 to 2.4 during the course of the experiment (Figure 4a).

The starting seawater solution has a $\delta^{26}\text{Mg}$ value of $-0.82\%e$. Samples that were taken during the execution of the experiment have slightly higher $\delta^{26}\text{Mg}$ values ranging from $-0.72\%e$ to $-0.76\%e$.

5. Discussion

5.1. Water-Rock Interaction at Macauley Volcano

Lithium and B isotope ratios in the acid-sulfate fluids from Macauley are lower than those of seawater and other acid-sulfate fluids (Wilckens et al., 2019), likely due to leaching of Li and B from a relative unaltered basement. The $\delta^{26}\text{Mg}$ values of Mg-enriched acid-sulfate fluids from Macauley are consistent with a seawater origin. Considering a typical $\delta^{26}\text{Mg}$ value of $-0.25\%e$ for the basement (i.e., Teng et al., 2010), addition of up to 17 mmol/kg Mg from the ocean crust should increase the $\delta^{26}\text{Mg}$ value of the fluid to $-0.72\%e$. Thus, leaching from the volcanic basement cannot explain the observed Mg enrichments. We rather suggest enrichments of Mg in the brine phase during phase separation and segregation without isotope fractionation. A lack of any correlation between Cl concentration and Mg isotope composition supports the findings of Eom et al. (2020) that phase separation does not affect the Mg isotope composition of vent fluids (Figure 3b).

![Figure 4](image-url)

**Figure 4.** (a) Evolution of Mg, $\text{SO}_4^{2-}$, and Ca concentrations as well as the pH of the fluids during the experiment showing a decrease in all species during heating to 350°C. (b) The increase of $\delta^{26}\text{Mg}$ and the simultaneous decrease in Mg concentrations during execution of the experiment implies incorporation of $^{24}\text{Mg}$ into precipitating Mg-phases. Red and blue lines are calculated compositions of fluid (solid line) and solid (dashed line) with a batch (B) and Rayleigh (R) fractionation model. The fraction of Mg in solution ($f_{\text{Mg}}$) is calculated using the initial fluid composition.

| Sample     | Comment          | Time (hr) | Ca (mM) | K (mM) | Mg (mM) | Sr (mM) | $\text{SO}_4^{2-}$ (mM) | pH     | $\delta^{26}\text{Mg} \pm 2\text{SD} (\%e)$ |
|------------|------------------|-----------|---------|--------|---------|---------|------------------------|--------|---------------------------------------------|
| SW Mg 000  | Cold @ 25°C      | 0         | 10.2    | 10.3   | 55.2    | 0.1     | 29.8                   | 7.5    | $-0.82 \pm 0.04$                          |
| SW Mg 001  | 350°C            | 3         | 1.0     | 10.2   | 42.3    | 0.0     | 10.1                   | 2.4    | $-0.73 \pm 0.04$                          |
| SW Mg 002  | 350°C            | 16.5      | 1.1     | 9.8    | 40.7    | 0.0     | 9.8                    | 2.4    | $-0.76 \pm 0.10$                          |
| SW Mg 003  | 350°C            | 23.5      | 1.1     | 10.2   | 41.8    | 0.0     | 10.0                   | 2.4    | $-0.72 \pm 0.06$                          |
| SW Mg 004  | 350°C            | 40.5      | 1.1     | 10.1   | 41.8    | 0.0     | 10.0                   | 2.4    | $-0.73 \pm 0.03$                          |

*Note. mM = mmol/kg.*
5.2. Water-Rock Interaction at Brothers Volcano

Calculated endmember Li and B isotope compositions of the high-temperature fluids from NW and Upper Caldera sites are within the range of other high temperature vent fluids from arc and back-arc settings (Araoka et al., 2016; Wilckens et al., 2018; Yamaoka et al., 2015). Using the data for fresh and altered dacite from Schlicht et al. (2022), modeling of B concentrations and isotope compositions of the fluid after water-rock interaction (see Wilckens et al., 2018; Yamaoka et al., 2015) shows further that the fluids reflect water-rock interaction between seawater and fresh dacite. δ²⁶Mg values from the caldera sites are also consistent with other high-temperature fluids from arc and backarc settings (Eom et al., 2020) and reflect incorporation of Mg into the ocean crust during hydrothermal circulation at high temperatures.

δ⁷Li and δ¹¹B values in the fluids from the Cone sites (Brothers volcano) are higher and imply limited water-rock interaction in the acid-sulfate fluids from Brothers. However, δ⁷Li values in the acid-sulfate fluids from the Cone sites are significantly lower than those from other acid-sulfate fluids within the Western Pacific (Wilckens et al., 2019), suggesting interaction with a less altered crust or a longer fluid residence time in the ocean crust. Figure 5 shows that the B and Li isotope composition of the Lower Cone fluids can be explained by two-component mixing between unmodified seawater and high-temperature vent fluid. Fluids from the Upper Cone have higher δ⁷Li values at similar δ¹¹B. Lower δ⁷Li values at constant δ¹¹B values could direct to a longer residence time in the ocean crust between venting and point of magmatic degassing at Lower Cone as suggested by de Ronde et al. (2011) and/or interaction with a less altered ocean crust at Lower Cone (Wilckens et al., 2019). Another plausible explanation is a decrease in δ¹¹B values due to admixture of a vapor phase containing B from a deep phase separation (de Ronde, Humphris, Höfig, et al., 2019; Stucker et al., 2022).

The Mg isotope composition of the acid-sulfate fluids from Upper Cone resembles seawater (Figure 3b). This agrees with the results of acid-sulfate fluids from DESMOS and North Su in the Manus Basin (Wilckens et al., 2019), consistent with a seawater origin of Mg. A minor enrichment of Mg due to phase separation that can be observed in the B isotope composition and in deep fluids from the IODP core (de Ronde, Humphris, & Höfig, 2019) is not influencing the Mg isotope composition, similar to Macauley volcano. In contrast, the Mg-enriched fluids from the Lower Cone are enriched in ²⁶Mg (Figure 3b). Stucker et al. (2022) discussed the dissolution of deep Mg-sulfate phases that formed from magmatic brines as a potential source of Mg enrichment in the Lower Cone fluids. The lack of an excess chlorinity in these fluids requires this deeply sourced Mg to be decoupled from chloride. This is difficult to achieve given the phase relations in the MgCl₂-MgSO₄-H₂O system, where the brines are always more rich in chloride than the coexisting salts (Balarew et al., 2001).

Kleint et al. (2019) discussed the dissolution of caminite as a potential source of the high Mg concentrations in the acid-sulfate fluids from Lower Cone. Although caminite was not found in any drill core from Brothers volcano (de Ronde, Humphris, Höfig, et al., 2019), we cannot exclude the possibility that caminite occurs in the volcanic basement at Lower Cone. The fluids from the Lower Cone in 2017 have lower pH values than fluids from the lower cone taken in 2004 and 2005 (de Ronde et al., 2011), which has been associated with an increased influx of magmatic gases. This could be related to temporal fluctuations in temperature and pH some time between 2005 and 2017, due to changes in the magmatic activity below Lower Cone, which may have favored precipitation of caminite in the ocean crust. A later decrease in temperature may have lead to redissolution of caminite. Unfortunately, the effect of caminite dissolution on the Mg isotope composition of the fluid is not well known, since no Mg isotope data for caminite is provided in the literature. Schmidt et al. (2019) suggested δ²⁶Mg values for caminite that are higher than those found in the ocean crust based on pore fluid data from the Terceira Rift, Azores. Using their minimum approximation of δ²⁶MgCaminite = −0.1‰, we can calculate the increase of δ²⁶Mg during dissolution of caminite for the fluids from Lower Cone using a simple mass balance approach. The calculated δ²⁶Mg values would yield about −0.5‰ for the Mg enriched fluids, which is significantly higher than the measured δ²⁶Mg value for the fluids (−0.62‰). This could either imply that Mg was not enriched by caminite dissolution in the fluids from Lower Cone, or that the δ²⁶Mg values estimated by Schmidt et al. (2019) are not

Figure 5. Boron versus lithium isotope ratios in acid-sulfate fluids from Upper and Lower Cone sites of Brothers volcano plotted together with a mixing line between seawater and high-temperature fluid end-member from NW caldera. The basement shows enriched δ⁷Li values in vent fluids from the Upper Cone, indicating a higher degree of alteration or a shorter residence time in the basement.
representative for caminite at Brothers volcano. To evaluate the δ²⁶Mg value of Caminite suggested by Schmidt et al. (2019) and to further quantify the Mg isotope fractionation during the precipitation of caminite, we thus conducted a seawater heating experiment.

5.3. Caminite Precipitation During the Heating of Seawater

Recent studies on the Mg isotope fractionation during precipitation of clay minerals and salts have shown that the magnitude and direction of isotope fractionation depends on the Mg-O bond length and the amount of water molecules that have to be dehydrated during the formation of the minerals, and that the magnitude of isotope fractionation, consistent with equilibrium fractionation, decreases with increasing temperatures (Hindshaw et al., 2020; Li et al., 2014; Shalev et al., 2021). In addition, pH values may also have an influence on the magnitude of Mg isotope fractionation, which has been explained by differences in octahedral bond length (Shalev et al., 2021). To study the isotopic fractionation during the precipitation of caminite and thus calculate potential caminite compositions in the volcanic basement at Lower Cone, we have chosen an experimental setup that is similar to natural conditions. Although caminite can precipitate at temperatures above 240°C (Haymon & Kastner, 1986; Janecky & Seyfried, 1983), the yield of caminite in experiments at similar temperatures is very low. To have higher yields of caminite precipitation, we thus chose a temperature of 350°C during heating of seawater.

5.3.1. Mass Balance and Thermodynamic Calculations

All fluid aliquots taken at different times during the experiment, had similar compositions, characterized by a decrease in Ca, Mg, and SO₄²⁻ and a drop in pH from 7.5 to 2.4 compared to the starting composition (Figure 4a). We hypothesize that these changes are due to the precipitation of anhydrite and caminite and tested the validity of this idea by mass balance calculations involving the fluid chemistry (see Table S1). First, the Ca loss was assumed to be due to the precipitation of anhydrite and so the equivalent molar quantity of sulfate was subtracted. Then the remaining SO₄²⁻ was used to precipitate caminite (MHS of composition Mg₁.₂₅SO₄(OH)₀.₅ × ₀.₅H₂O of Janecky & Seyfried, 1983) with the corresponding quantities of Mg removed from the fluid composition. The results of the mass balance calculations indicate that the changes in the concentrations observed can be very well explained by the precipitation of anhydrite and caminite.

The speciation of the fluid and mineral-solution equilibria were computed for 350°C and 500 bar using The Geochemist Workbench and a thermodynamic database tailor-made using SUPCRT92 (Johnson et al., 1992; see Supporting Information S1). Calcium, Mg and sulfate concentrations and pH values agree with the measurements presented in Section 4.2. The abundance of the minerals predicted in the model agrees with the mass balance constraints. We conclude that (a) precipitation of anhydrite and caminite can fully explain the observed changes in fluid composition after heating to 350°C, and (b) equilibrium state was virtually reached in the experiment.

5.3.2. Mg Isotope Fractionation During Heating of Seawater

Aliquots of fluid that were collected during the experiment have slightly higher δ²⁶Mg values compared to the starting solution, implying Mg isotope fractionation between the precipitated Mg-bearing phases and seawater (Figure 4b). The evaluation of the seawater heating experiments implies that caminite is the main Mg-bearing phase precipitating during heating of seawater to temperatures of 350°C. Even if minor amounts of brucite precipitated, this would not affect the δ²⁶Mg value of the fluid, as Li et al. (2014) observe a decrease in Mg isotope fractionation during brucite formation with increasing temperatures (Δ²⁶Mgbrucite-Mg²⁺ = 0‰ at 40°C). Therefore, we suggest, that the observed shift in δ²⁶Mg is solely related to Mg isotope fractionation during precipitation of caminite. After caminite precipitation, the fluid becomes enriched in ²⁶Mg, implying a preferential incorporation of ²⁴Mg into the precipitating caminite during heating of seawater. Since the formation of caminite in hydrothermal systems is associated with the heating of seawater (Bischoff & Seyfried, 1978), we can infer the Mg isotope composition of natural caminite occurring at Brothers volcano from the experimental results. To estimate the potential Mg isotope composition of caminite at Brothers volcano, we assume that caminite has been precipitated prior to acid-sulfate venting during heating of seawater to temperatures above 350°C. Due to the young age of the Kermadec volcanoes (<0.77 Ma; Wright et al., 1994) and the hydrothermal system at the cone sites from Brothers volcano in particular (Caratori Tontini et al., 2012; de Ronde et al., 2005), and the long residence time of Mg in seawater of about 10 million years (and therefore a quite stable δ²⁶Mg value of seawater) (Berner & Berner, 2012), we can use the present-day Mg isotope composition of seawater (−0.87‰) to calculate the caminite composition. Considering α²⁶Caminite-SW of 0.9997–0.9998 as observed in the experiment, the precipitating
caminite would have $\delta^{26}\text{Mg}$ values between $-1.2\%$ and $-0.9\%$, depending on the fraction of caminite being precipitated (Figure 4b). Dissolution of caminite will thus lead to a decrease in $\delta^{26}\text{Mg}$ values of the fluid and the trend toward higher $\delta^{26}\text{Mg}$ values with increasing Mg concentration in the fluids from the Lower Cone cannot be explained by the dissolution of caminite as suggested by Kleint et al. (2019). Considering caminite precipitation at lower temperatures, this should result in even lower $\delta^{26}\text{Mg}$ values for caminite, while at precipitation temperatures $>350^\circ\text{C}$ $\alpha\text{Caminite-SW}$ will converge to values of about 1 as isotope fractionation decreases with increasing temperature. Therefore, the experimental results imply that the Mg-enriched fluids from Lower Cone cannot be explained by caminite dissolution. Differences in the Mg isotope composition of caminite between the experimental results and the estimated data by Schmidt et al. (2019) may be due to different precipitation conditions (e.g., pH and temperature) or precipitation from an $^{24}\text{Mg}$ enriched fluid at the Terceira Rift.

5.4. Mg Leaching During (Advanced) Argillic Alteration

The high acidity and high concentrations of magmatic volatiles in acid-sulfate fluids change the style of basement alteration during water-rock interaction. High-temperature hydrothermal water-rock interaction produces alteration assemblages characterized by the formation of Mg-rich clay minerals (i.e., chlorite, smectite, and saponite), phyllosilicates, albite and quartz as well as sulfates and sulfides (i.e., Bach et al., 2013; cf. NW Caldera site; de Ronde, Humphris, Höfig, et al., 2019). By contrast, water-rock interaction with acid-sulfate fluids produce advanced argillic alteration assemblages, such as quartz, illite, pyrophyllite, diaspore, alunite, and anhydrite (de Ronde, Humphris, & Höfig, 2019; de Ronde, Humphris, Höfig, et al., 2019; Gena et al., 2001; Lackschewitz et al., 2004). Thus, rocks with advanced argillic mineral assemblages are highly depleted in MgO.

Altered rocks recovered from drilling of the Upper Cone at Brothers volcano show three different alteration assemblages with variable proportions of illite, natroalunite, pyrophyllite, quartz, opal CT, pyrite, and native sulfur (de Ronde, Humphris, & Höfig, 2019; de Ronde, Humphris, Höfig, et al., 2019). All of these alteration assemblages show an extreme depletion in MgO (de Ronde, Humphris, & Höfig, 2019). This loss of Mg from the altered volcanic basement at the Upper Cone site can be explained by Mg leaching due to acid-sulfate alteration. The seawater-like Mg composition of the fluids from the Upper Cone indicate that Mg is neither added to, nor lost, from the hydrothermal fluid, because the host rock is mainly altered and largely devoid of Mg (de Ronde, Humphris, & Höfig, 2019). The Lower Cone is built on top of the northeastern flank of the Upper Cone and is thus potentially younger and host to a younger venting system than the Upper Cone (Caratori Tontini et al., 2019; de Ronde, Humphris, Höfig, et al., 2019). Thus, the host rock at the Lower Cone may be less altered compared to the Upper Cone, and is more obviously affected by leaching associated with the acid-sulfate fluids, which could explain both, the Mg enrichment and lower $\delta^7\text{Li}$ values in the fluids at the Lower Cone. Mass balance calculations imply a $\delta^{26}\text{Mg}$ value of about $-0.3\%$ for the source of Mg added to the fluids from Lower Cone, which is in the range mid ocean ridge basalts and ocean island basalts (J. Huang et al., 2015). Although $\delta^{26}\text{Mg}$ values in arc lavas are generally higher due to addition of heavy Mg from the subduction of altered oceanic crust and sediments (Teng et al., 2016), we cannot exclude this hypothesis as altered oceanic crust can also be enriched in light Mg isotopes. Therefore, the most likely explanation to explain the enrichment of Mg in the fluids from Lower Cone is a combination of (a) dissolution of caminite and (b) leaching of Mg from the basement. Further analyses of Mg isotopes in fresh and altered basement rocks from Brothers volcano could help to prove this theory.

6. Summary and Conclusion

This study demonstrates the use of Mg isotopes to decipher the origin of Mg in hydrothermal vent fluids. Differences in the Mg isotope signature of acid-sulfate fluids from Macauley and Brothers volcano reflect variable sources for Mg at both locations. Mg-enriched fluids from Macauley have Mg isotope compositions that are consistent with a seawater composition and thus can be explained by venting of a Mg-rich brine phase that formed during phase separation and segregation without significant water-rock interaction. These results support earlier findings that Mg isotopes do not fractionate during phase separation.

Seawater-like Mg isotope compositions with minor Mg enrichments in the acid-sulfate fluids from the Upper Cone site at Brothers volcano are similar to other acid-sulfate fluids from the Pacific, also supporting a lack of Mg isotope fractionation during phase separation. By contrast, the Mg-enriched acid-sulfate fluids from the Lower Cone site are enriched in $^{26}\text{Mg}$ compared to seawater, which can be explained by a combination of caminite
dissolution and Mg leaching during argillic alteration of the ocean crust. After experimental investigation on Mg isotope fractionation during precipitation of caminite from seawater, exclusive dissolution of caminite was disproved as it could not explain the higher Mg isotope compositions in the fluids from Lower cone. Instead, similar B but different Li isotope composition in the acid-sulfate fluids show differences in the host rock alteration at the Cone sites with a less altered basement (i.e., lower δ7Li values) postulated for the Lower Cone. As Mg gets depleted in the basement during alteration by acid-sulfate fluids (i.e., Upper Cone), less altered rocks of the Lower Cone would constitute the source of Mg-rich fluids. This is consistent with studies that show a younger age (and potentially a less altered basement) for the Lower Cone.

Based on the current data, the most plausible explanation of the elevated SO2−4 concentration at Lower Cone originates from (a) SO2 disproportionation of magmatic gases, and (b) dissolution of alunite (and caminite). The elevated Mg levels in the Lower Cone fluids can be explained by (a) Mg leaching from the volcanic host rock during acid-sulfate alteration (leading to higher δ26Mg values in the fluids), and (b) minor caminite dissolution (with a seawater-like Mg isotope signature).

Data Availability Statement

The data is archived in Pangaea®—Data Publisher for Earth and Environmental Sciences (https://doi.org/10.1594/PANGAEA.949806 and https://doi.org/10.1594/PANGAEA.949807).

References

Araoka, D., Nishio, Y., Gamo, T., Yamasaka, K., & Kawahata, H. (2016). Lithium isotope systematics of submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific. Geochemistry, Geophysics, Geosystems, 17(10), 3835–3853. https://doi.org/10.1002/2016gc006355

Bach, W., Jons, N., & Klein, F. (2013). Metasomatism within the ocean crust. In D. E. Harlov & H. Austrheim (Eds.), Metasomatism and the chemical transformation of rock (pp. 253–288). Springer Berlin Heidelberg.

Baker, E. T., Walker, S. L., Embley, R. W., & de Ronde, C. E. J. (2012). High-resolution hydrothermal mapping of Brothers caldera, Kermadec arc. Economic Geology, 107(8), 1583–1593. https://doi.org/10.2113/eg2017.107.1583

Balarew, C., Tepavitcharova, S., Rabadjieva, D., & Voigt, W. (2001). Solubility and crystallization in the system MgCl2–MgSO4–H2O at 50 and 75°C. Journal of Solution Chemistry, 30(9), 815–823. https://doi.org/10.1023/a:1012288316884

Barker, S. J., Wilson, C. J. N., Baker, J. A., Millet, M.-A., Rotella, M. D., Wright, I. C., & Wysoczanski, R. J. (2013). Geochemistry and petrogenesis of silicic magmas in the intra-oceanic Kermadec arc. Journal of Petrology, 54(2), 351–391. https://doi.org/10.1093/petrology/egt071

Berkenbosch, H. A., de Ronde, C. E. J., Gemmell, J. B., McNeill, A. W., & Goernann, K. (2012). Mineralogy and formation of black smoker chimneys from Brothers submarine volcano, Kermadec arc. Economic Geology, 107(8), 1613–1633. https://doi.org/10.2113/eg2017.107.1613

Berkenbosch, H. A., de Ronde, C. E. J., Paul, B. T., & Gemmell, J. B. (2015). Characteristics of Cu isotopes from chalcopyrite-rich black smoker chimneys at Brothers volcano, Kermadec arc, and Niuatahi volcano, Lau basin. Mineralium Deposita, 50(7), 811–824. https://doi.org/10.1007/s00126-014-0571-y

Berner, K. E., & Berner, R. A. (2012). Global environment: Water, air, and geochemical cycles (p. 488). Princeton University Press.

Bischoff, J. L., & Seyfried, W. E. (1978). Hydrothermal chemistry of seawater from 25°C to 350°C. American Journal of Science, 278(6), 838–860. https://doi.org/10.2475/ajs.278.6.838

Butterfield, D. A., Nakamura, K. I., Takano, B., Lillley, M. D., Lupton, J. E., Resing, J. A., & Roe, K. K. (2011). High SO2 flux, sulfur accumulation, and gas fractionation at an erupting submarine volcano. Geology, 39(9), 803–806. https://doi.org/10.1130/g31901.1

Caratori Tontini, F., Tivey, M. A., de Ronde, C. E. J., Humphris, S. E., & Höfig, T. W. (2019). Heat flow and near-seafloor anomalies highlight hydrothermal circulation at Brothers volcano caldera, southern Kermadec arc, New Zealand. Geophysical Research Letters, 46(14), 8252–8260. https://doi.org/10.1029/2019gl083517

Dämmer, L. K., van Dijk, I., de Nooijer, L., van der Wagt, B., Wielkens, F. K., Zoetemelk, B., & Reichard, G.-J. (2021). Temperature impact on magnesium isotope fractionation in cultured foraminifera. Frontiers in Earth Sciences – Biogeoscience, 9, 642256. https://doi.org/10.3389/feart.2021.642256

DeMets, C., Gordon, R. G., & Argus, D. F. (2010). Geologically current plate motions. Geophysical Journal International, 181(1), 1–80. https://doi.org/10.1111/j.1365-246X.2009.04491.x

DeMets, C., Gordon, R. G., Argus, D. F., & Stein, S. (1994). Effect of recent revisions to the geomagnetic reversal time scale on estimates of current plate motions. Geophysical Research Letters, 21(20), 2191–2194. https://doi.org/10.1029/94gl02118

de Ronde, C. E. J., Baker, E. T., Massoth, G. J., Lupton, J. E., Wright, I. C., Feely, R. A., & Greene, R. G. (2001). Intra-ocenaeic subduction-related hydrothermal venting, Kermadec volcanic arc, New Zealand. Earth and Planetary Science Letters, 193(3–4), 359–369. https://doi.org/10.1016/s0012-821x(01)00534-9

de Ronde, C. E. J., Baker, E. T., Massoth, G. J., Lupton, J. E., Wright, I. C., Sparks, R. J., et al. (2007). Submarine hydrothermal activity along the mid-Kermadec Arc, New Zealand: Large-scale effects on venting. Geochemistry, Geophysics, Geosystems, 8(7), Q07007. https://doi.org/10.1029/2006GC001495

de Ronde, C. E. J., Hannington, M. D., Stoffers, P., Wright, I. C., Ditchburn, R. G., Reyes, A. G., et al. (2005). Evolution of a submarine magmatic-hydrothermal system: Brothers volcano, southern Kermadec arc, New Zealand. Economic Geology, 100(6), 1097–1133. https://doi.org/10.2113/gsecongeo.100.6.1097

de Ronde, C. E. J., Humphris, S. E., & Höfig, T. W. (2019). Brothers arc flux. International Ocean Discovery Program.
Seyfried, W. E. (1987). Experimental and theoretical constraints on hydrothermal alteration processes at mid-ocean ridges. *Annual Review of Earth and Planetary Sciences, 15*(1), 317–335. https://doi.org/10.1146/annurev.eu.15.050187.001533

Seyfried, W. E., & Bischoff, J. L. (1979). Low temperature basalt alteration by sea water: An experimental study at 70°C and 150°C. *Geochimica et Cosmochimica Acta, 43*(12), 1937–1947. https://doi.org/10.1016/0016-7037(79)90006-1

Seyfried, W. E., & Mottl, M. J. (1982). Hydrothermal alteration of basalt by seawater under seawater-dominated conditions. *Geochimica et Cosmochimica Acta, 46*(6), 985–1002. https://doi.org/10.1016/0016-7037(82)90054-0

Shalev, N., Lazar, B., Halicz, L., & Gavriel, I. (2021). The Mg isotope signature of marine Mg-evaporites. *Geochimica et Cosmochimica Acta, 301*, 30–47. https://doi.org/10.1016/j.gca.2021.02.032

Stucker, V. K., de Ronde, C. E. J., Laurence, K. L., & Phillips, A. M. (2022). Rare time series of hydrothermal fluids for a submarine volcano: 14 years of vent fluid compositions for Brothers Volcano, Kermadec Arc New Zealand. *Economic Geology*. https://doi.org/10.5382/econgeo.4922

Stucker, V. K., Walker, S. L., de Ronde, C. E. J., Caratori Tontini, F., & Tsuchida, S. (2017). Hydrothermal venting at Hinepuia submarine volcano, Kermadec arc: Understanding magmatic hydrothermal fluid chemistry. *Geochemistry, Geophysics, Geosystems, 18*(10), 3646–3661. https://doi.org/10.1002/2016GC006713

Teng, F.-Z., Hu, Y., & Chauvel, C. (2016). Magnesium isotope geochemistry in arc volcanism. *Proceedings of the National Academy of Sciences, 113*(26), 7082–7087. https://doi.org/10.1073/pnas.1518456113

Teng, F.-Z., Li, W.-Y., Ke, S., Marty, B., Dauphas, N., Huang, S., et al. (2010). Magnesium isotopic composition of the Earth and chondrites. *Geochimica et Cosmochimica Acta, 74*(14), 4150–4166. https://doi.org/10.1016/j.gca.2010.04.019

Timm, C., Davy, B., Haase, K., Hoernle, K. A., Graham, I. J., de Ronde, C. E. J., et al. (2014). Subduction of the oceanic Hikurangi Plateau and its impact on the Kermadec Arc. *Nature Communications, 5*(1), 4923. https://doi.org/10.1038/ncomms5923

Voigt, M., Pearce, C. R., Fries, D. M., Baldermann, A., & Oelkers, E. H. (2020). Magnesium isotope fractionation during hydrothermal seawater-basalt interaction. *Geochimica et Cosmochimica Acta, 272*, 21–35. https://doi.org/10.1016/j.gca.2019.12.026

Von Damm, K. L., Edmond, J. M., Measures, C. I., & Grant, B. (1985). Chemistry of submarine hydrothermal solutions at Guaymas basin, Gulf of California. *Geochimica et Cosmochimica Acta, 49*(11), 2221–2237. https://doi.org/10.1016/0016-7037(85)90223-6

Wilckens, F. K., Reeves, E. P., Bach, W., Meixner, A., Seewald, J. S., & Kasemann, S. A. (2018). The influence of magmatic fluids and phase separation on B systematics in submarine hydrothermal vent fluids from back-arc basins. *Geochemistry, Geophysics, Geosystems, 19*(10), 3646–3661. https://doi.org/10.1002/2016GC006713

Wilckens, F. K., Reeves, E. P., Bach, W., Seewald, J. S., & Kasemann, S. A. (2019). Application of B, Mg, Li, and Sr isotopes in acid-sulfate vent fluids and volcanic rocks as tracers for fluid-rock interaction in back-arc hydrothermal systems. *Geochemistry, Geophysics, Geosystems, 20*(12), 5849–5866. https://doi.org/10.1029/2019gc008694

Wright, I. C., & Gamble, J. A. (1999). Southern Kermadec submarine caldera arc volcanoes (SW Pacific): Caldera formation by effusive and pyroclastic eruption. *Marine Geology, 161*(1–4), 207–227. https://doi.org/10.1016/S0025-3227(99)00040-7

Wright, I. C., Worthington, T. J., & Gamble, J. A. (2006). New multibeam mapping and geochemistry of the 30°–35°S sector, and overview, of southern Kermadec arc volcanism. *Journal of Volcanology and Geothermal Research, 149*(3–4), 263–296. https://doi.org/10.1016/j.jvolgeores.2005.03.021

Yamaoka, K., Hong, E., Ishikawa, T., Gamo, T., & Kawahata, H. (2015). Boron isotope geochemistry of vent fluids from arc/back-arc seafloor hydrothermal systems in the western Pacific. *Chemical Geology, 392*, 9–18. https://doi.org/10.1016/j.chemgeo.2014.11.009