Origin of High Mg and SO₄ Fluids in Sediments of the Terceira Rift, Azores-Indications for Caminite Dissolution in a Waning Hydrothermal System

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Abstract During R/V Meteor cruise 141/1, pore fluids of near surface sediments were investigated to find indications for hydrothermal activity in the Terceira Rift (TR), a hyperslow spreading center in the Central North Atlantic Ocean. To date, submarine hydrothermal fluid venting in the TR has only been reported for the D. João de Castro seamount, which presently seems to be inactive. Pore fluids sampled close to a volcanic cone at 2,800-m water depth show an anomalous composition with Mg, SO₄, and total alkalinity concentrations significantly higher than seawater and a nearby reference core. The most straightforward way of interpreting these deviations is the dissolution of the hydrothermally formed mineral caminite (MgSO₄·0.25 Mg(OH)₂·0.2H₂O). This interpretation is corroborated by a thorough investigation of fluid isotope systems (δ²⁶Mg, δ³⁰Si, δ³⁴S, δ³⁴/³²Ca, and ⁸⁷Sr/⁸⁶Sr). Caminite is known from mineral assemblages with anhydrite and forms in hydrothermal recharge zones only under specific conditions such as high fluid temperatures and in altered oceanic crust, which are conditions generally met at the TR. We hypothesize that caminite was formed during hydrothermal activity and is now dissolving during the waning state of the hydrothermal system, so that caminite mineralization is shifted out of its stability zone. Ongoing fluid circulation through the basement is transporting the geochemical signal via slow advection toward the seafloor.

Plain Language Summary Hydrothermal vents are a common phenomenon in oceanic spreading centers worldwide. During Meteor cruise 141/1 we sampled sediments and extracted pore fluids to find the first indications for hydrothermal activity in the Terceira Rift. The results indicate that a hydrothermal vent close to a major volcanic cone formed in the past and seems to be in a waning state at present. Sampled fluids are enriched in total alkalinity, Mg and SO₄. We found that the most straightforward explanation for this unusual finding is the dissolution of the hydrothermally formed mineral caminite, a magnesium-sulfate-hydroxide-hydrate. Caminite is a rare mineral but suggested to be abundant under specific conditions in hydrothermal recharge zones. We propose that caminite formed in the Terceira Rift is now dissolving as temperatures decline, and fluids enriched in Mg and SO₄ are transported along deep-rooted faults to the seafloor.

1. Introduction

Hydrothermal vents are common phenomena in slow- to fast-spreading centers worldwide (Beaulieu et al., 2013). Numerous authors provide a wealth of data on mineral assemblages and fluid chemistry of hydrothermal systems and their recharge zones (e.g., Alt, 1995; Teagle et al., 1998). Hydrothermal fluid circulation is a driver for cooling of the Earth’s crust and also plays a major role in geochemical fluxes (Elderfield & Schultz, 1996). Generally, high-temperature reactions are the reason that fluids become depleted in Mg and SO₄ while Ca and fluid-mobile elements like Li are enriched. Mg is quantitatively removed from fluids by the formation of Mg-rich smectite such as saponite (Alt & Honnorez, 1984). SO₄ in hydrothermal systems can undergo various reactions. At temperatures above 150 °C, SO₄ is typically removed by the precipitation of anhydrite (Alt et al., 1986; Teagle et al., 1998). However, SO₄ can also be reduced and precipitate as sulfide mineral (Alt, 1995). Ca is leached from the basement during albition of plagioclase (Alt et al., 1986;
Levels of enrichment can vary, but concentrations of Ca in fluids can reach up to 80 mM (e.g., Butterfield et al., 1994). There are few studies focusing on mineral dissolution after cooling of hydrothermal fluid circulation (e.g., Gieskes et al., 2002; Gruen et al., 2014), leading to substantial changes in fluid compositions (e.g., enrichment in SO₄ and Ca due to anhydrite dissolutions, brine formation due to leaching of hydrothermally formed salts in the subsurface).

The Terceira Rift (TR) is a ~500 km WNW-ESE striking rift in the Central North Atlantic Ocean, marking the plate boundary between Nubia and Eurasia. The TR has been described as a hyperslow spreading center with a spreading rate of 4 mm a⁻¹ (Vogt & Jung, 2004). Cutting through the Azores Plateau, the TR comprises four basins and passes through three volcanic islands of the Azores Archipelago (Figure 1). Albeit ongoing magmatic activity in this region, only nine onshore hydrothermal springs (Couto et al., 2015), and one offshore submarine vent, located at the D. João de Castro seamount (Figure 1), have been reported to date (Figure 1; Cardigos et al., 2005). However, during a previous Meteor expedition (M 128) in 2016 no signs of hydrothermal activity was detected at this location (Beier, 2016). Weiß et al. (2015) reported on 252 volcanic cones and sills in the eastern TR and the flanks of São Miguel, which possibly could host...
hydrothermal systems. In the southern Hirondelle Basin major volcanic cones are connected to listric faults along the rift axis of the TR (Figure 1c), providing a potential pathway for the ascent of hydrothermal fluids to the seafloor. One of the major cones shows no sediment cover in the backscatter data (Weiß et al., 2015), which can be regarded as sign for recent magmatic activity. This volcanic cone provides presumably good preconditions to host a hydrothermal system. During R/V Meteor cruise M141/1 in September 2017 we sampled pore fluids by gravity coring in the vicinity of the elongated volcanic cone to detect potential signs of ongoing hydrothermal activity in the TR.

2. Materials and Methods

2.1. Pore Fluid and Sediment Sampling

Two gravity cores (GCs) were retrieved during the cruise at 2,800-m water depth. GC51 was taken on the fault close to the volcanic cone whereas GC50 was taken as a regional reference core (Figures 1b and 1c). Both GCs had a length of 5.75 m and were equipped with a plastic liner. Right after retrieval on deck, the plastic liner was cut into 1-m-long segments and head space samples for hydrocarbon gas analyses were taken. The sampling interval was between 5 and 20 cm. Sediment samples were squeezed in a cold room with an argon gas squeezer. On average, squeezing took about 10 min. Gas pressure was usually up to 5 bar. The pore fluid was filtered through 0.2-μm cellulose Whatmann filters.

2.2. Pore Fluid Analyses

On board analyses for total alkalinity (TA) were carried out using a METROHM titration unit 876 Dosimat plus. TA was determined by titration with 0.02 N HCl using a methyl red indicator. The solution was bubbled with argon to remove CO₂ gas released during the titration. On board analyses for NH₄ were carried out using a Hitachi U2800A spectrophotometer applying a calibration curve with eight standards covering the concentration range between 0 and 332.62 μM. In our shore-based laboratories at GEOMAR Helmholtz Center for Ocean Research, Kiel, cation concentrations (B, Ba, Ca, K, Li, Mg, Na, Si, and Sr) were determined using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, JY 170 Ultrace, Jobin Yvon). Anion concentrations (Cl, Br, and SO₄) were analyzed using the Ion Chromatography (761 IC-Compact, Methrom). The IAPSO seawater standard was used to check the reproducibility and accuracy of the ICP-OES and IC chemical analyses (supplemental data; Gieskes et al., 1991). The reproducibility is in general better than 1% relative standard deviation (RSD) for each element. Detailed description of the methods can be found in for example, Hensen et al. (2007) and Scholz et al. (2009).

2.3. Solid Phase Analyses

Sediment samples from both cores were taken to determine their porosity, water content, chemical bulk analyses, and petrological description (see Tables S3 and S4 in the supporting information). For the chemical bulk analyses, sediments were dried at 65 °C for 24 hr and homogenized. One hundred milligrams of each sample was filled into a Savillex vessel and treated with 2 cm³ HF, 2 cm³ HNO₃, and 3 cm³ HClO₄ at 185 °C for 8 hr. Another 1 cm³ of HNO₃ was added to smoke off the acid. The full method description is available in Scholz et al. (2016). After treatment with acids, sediment samples were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) at GEOMAR, for concentrations of Al, Ca, Fe, K, Mg, Na, and Sr. The reproducibility is better than 1% RSD.

2.4. Smear Slides

Modal compositional data were obtained by counting at least 400 points in each of the 13 selected smear slides with a modified Gazzi-Dickinson method based on Decker and Helmold (1985) and von Eynatten and Gaupp (1999) using a microstep point-counting system and the Petroglide software without distinguishing into grain size fractions. The amount of 400 points was selected to derive a statistically significant estimation (e.g., Van der Plas & Tobi, 1965) of respective volume percentages of the components in the sediments. We distinguish between 13 juvenile and nonjuvenile components. On the basis of common features four characteristic groups (total glass, total lithics, microfossils, and clay) were defined. Volume percentages of components or modal groups given in the text are normalized to 100%. Percentage raw data and calculated volume percentages of modal groups are listed in Tables S6 and S7 in the supporting information. Minerals like pyroxene, feldspar, amphibole, different types of pyroclasts, and sedimentary and volcanic lithics have not been subdivided in different species. Biogenic material has been subdivided into the main components.
Table 1
Pore Fluid Data GC50

| Depth (cm) | NH4 (μM) | TA (meq/L) | B (mM) | Ca (mM) | Na (mM) | Mg (mM) | Sr (μM) | Si (mM) | Li (μM) | K (mM) | Cl (mM) | SO4 (mM) | Porosity (–) |
|-----------|---------|-----------|-------|--------|--------|--------|--------|--------|--------|-------|--------|--------|------------|
| 12        | 11.40   | 2.99      | 0.464 | 10.68  | 483    | 53.8   | 87.2   | 0.19   | 28.1   | 10.7  | 559.7  | 28.6   | –          |
| 23        | 39.85   | 3.06      | 0.458 | 10.88  | 484    | 54.4   | 88.7   | 0.21   | 27.2   | 10.7  | 566.8  | 29.3   | 0.65       |
| 48        | 89.19   | 3.27      | 0.465 | 10.63  | 487    | 54.8   | 88.1   | 0.25   | 27.2   | 10.8  | 572.8  | 29.4   | 0.62       |
| 60        | 113.00  | 3.20      | 0.440 | 10.08  | 481    | 53.3   | 85.7   | 0.25   | 24.9   | 10.7  | 569.1  | 28.4   | –          |
| 71        | 123.80  | 3.20      | 0.445 | 9.81   | 480    | 52.8   | 85.7   | 0.25   | 25.0   | 10.7  | 568.7  | 28.5   | –          |
| 85        | 159.90  | 3.58      | 0.467 | 10.29  | 487    | 54.7   | 88.7   | 0.23   | 26.3   | 10.8  | 574.9  | 29.2   | 0.62       |
| 108       | 186.30  | 3.71      | 0.476 | 10.02  | 486    | 54.7   | 88.1   | 0.22   | 25.7   | 10.6  | 572.5  | 28.6   | 0.82       |
| 118       | 188.10  | 3.63      | 0.455 | 9.72   | 483    | 53.6   | 85.9   | 0.21   | 24.1   | 10.2  | 569.1  | 28.4   | –          |
| 133       | 194.10  | 3.84      | 0.487 | 9.82   | 484    | 54.4   | 86.7   | 0.22   | 25.1   | 10.5  | 572.8  | 28.7   | 0.64       |

Note. Core Location: 37°58.345′N; 26°5.046′W; gray areas indicate ash and tephra layers.

(nannofossils and foraminifers), and minor abundances have been summarized in “biogenic rest.” The reproducibility (2 times counting) was tested for two different samples and is better than 4% RSD regarding the modal groups. A detailed description can be found in the supporting information.

### 2.5. Si Isotopes

Pore fluid samples were prepared for Si isotope measurements following the purification method of Georg et al. (2006). The samples were loaded onto 1-ml precleaned cation-exchange resin (Biorad AG50 W-X8) and eluted with 2-ml Milli-Q water. Si isotopes were measured on the NuPlasma high-resolution Multicollector-Inductively Coupled Plasma Mass Spectrometer (HR MC-ICPMS) in medium resolution mode using the Cetac Aridus II desolator at GEOMAR. The Si concentration after sample purification equaled ~22 μM, yielding Si recoveries of ≥99% and a procedural blank below detection limit. The measurements were executed using the standard sample bracketing method to account for mass bias drifts of the instrument (Albarède et al., 2004). Si isotopes are given in the δ30Si notation, which represents the deviation of the sample 30Si/28Si from that of the international Si standard NBS28. Long-term δ30Si values of the reference materials Big Batch (~10.6 ± 0.2‰; 2 SD; n = 49), IRMM018 (~1.5 ± 0.2‰; n = 48), and Diatomite (+1.3 ± 0.2‰; 2 SD; n = 44) agree well with published δ30Si values in the literature (e.g., Reynolds et al., 2007). Additionally, an in-house pore fluid matrix standard has been measured, which yielded an average δ30Si value of +1.3 ± 0.2‰ (2 SD; n = 17). All samples were measured 2–3 times on different days and the resulting δ30Si values have uncertainties between 0.1 and 0.2‰ (2 SD).

### 2.6. Sulfur Isotopes

Pore fluids were filtered (0.2-μm pore size filter) and acidified (25% HCl) to a pH below 2. Subsequently, BaCl2 solution (8.5%) was added to precipitate barium sulfate at 80 °C. The BaSO4 precipitate was obtained via filtration using a cellulose nitrate filter (0.45-μm pore size). For δ34S measurement 0.4-mg barium sulfate mixed with 0.4- to 0.8-mg V2O5 (catalyst) was placed into tin capsules. The δ34S values were determined using an EA-IRMS (Thermo Scientific Delta V advantage coupled with a Flash-EA-Isolink-CN Elemental Analyzer) at the Institute of Geology, Westfälische Wilhelms-Universität of Münster, and are reported in the standard delta notation as per mil difference to the Vienna-Canyon Diablo Troilite (V-CDT) standards. Analytical performance was monitored using international reference materials IAEA S-1, S-2, S-3, and NBS 127 with an external reproducibility better than 0.6‰ (2 SD). For δ18O_SO4 analysis 0.2-mg barium sulfate was placed in a silver capsule, and δ18O_SO4 was determined with a TC/EA-IRMS (Thermo Scientific Delta V plus connected with a high-temperature pyrolysis unit). The δ18O_SO4 values are reported as per mil difference to the V-SMOW standard. Measurement of replicate samples and reference materials (IAEA-SO-5, IAEA-SO-6, and NBS 127) yielded an external reproducibility better than 1.0‰ (2 SD).

### 2.7. Sr Isotopes

Sr isotope ratios (δ87Sr/86Sr) were measured by thermal ionization mass spectrometry (TIMS, TRITON, ThermoFisher Scientific) at the GEOMAR on aliquots of the original ICP-OES pore water samples.
(described above). According to the prior element concentration analyses (ICP-OES) individual sample amounts equivalent to ~1,500 ng Sr (usually in the range of tens to hundreds of μl pore water) were dried down in 2 ml of a 1 plus 2 mixture of 30% H2O2 (supra pure) and 8 N HNO3 (double distilled from per analyses quality). The separation of Sr followed a highly selective one step ion exchange chromatography using SrSpec resin (Eichrom) at whole procedure blanks of max. 60 pg. Before loading 100 to 200 ng Sr mixed with TaCl5 activator on Re single filaments for TIMS measurements the Sr eluate was dried down in the H2O2/HNO3 mixture as described above. Repeated analyses of the standard NIST SRM 987 were used for performance monitoring and normalization of the measured 87Sr/86Sr ratios applying a standard value of 0.710248 and reaching a reproducibility of ±0.000010 (2 SD, n = 10) throughout the study. The latter level of precision is representative for the individual sample results (see uncertainties given in Table 2 and Table 4). Furthermore, the IAPSO seawater standard a87Sr/86Sr ratio was determined on 0.709178 at ±0.000010 (2 SD, n = 4).

2.8. Ca Isotopes

Ca isotope measurements were performed on aliquots of the original pore water samples used for Sr isotope and element geochemistry ICP-OES analyses, with the same pretreatment as described for Sr purification. Calcium yields were >95% suggesting that Ca isotopes are not measurably fractionated by chemical purification (Morgan et al., 2011).

Prior to Ca isotope measurements samples were purified to remove matrix and interfering elements. We used a fully automated chromatographic purification system (prepFAST MC, ESI, Omaha, Nebraska, USA) following the method of Romaniello et al. (2015).

Caclide isotope measurements were performed on a MC-ICPMS (Thermo Scientific Neptune, Thermo Fisher Scientific, Bremen, Germany) at the mass spectrometer facilities of GEOMAR. The mass spectrometer was set up to measure m/z of 42, 43, 43.5, and 44 simultaneously. In order to suppress interfering Ca- and Ar-hydrides (e.g., 40Ar3H2 on 42Ca) an APEX IR (ESI, Omaha, Nebraska, USA) sample introduction system was used. All measurements were performed in medium resolution (MR, m/Δm ~4,000) on the low mass side of the peaks (cf. Wieser et al., 2004).

Instrumental fractionation (mass bias) was corrected by applying the standard-sample-bracketing (SSB) approach. Interference correction for remaining sample Sr was done following the method of Morgan et al. (2011). Ca isotopes are given in the δ54/42Ca notation, which represents the deviation of the sample

### Table 2

| Depth (cm) | NH4 (μM) | TA (meq/L) | B (mM) | Ca (mM) | Na (mM) | Mg (mM) | Sr (μM) | Si (mM) | Li (μM) | K (mM) | Cl (mM) | SO4 (mM) | Porosity (−) |
|-----------|----------|------------|-------|---------|---------|---------|--------|--------|--------|-------|--------|---------|-------------|
| 16        | 64.57    | 4.05       | 0.448 | 10.66   | 485     | 55.7    | 101.8  | 0.21   | 29.5   | 10.3  | 560.6  | 29.5    | 0.59        |
| 30        | 88.09    | 4.67       | 0.452 | 10.41   | 481     | 55.5    | 109.6  | 0.22   | 28.9   | 9.8   | 564.7  | 29.4    |             |
| 40        | 114.50   | 4.94       | 0.473 | 10.79   | 490     | 57.4    | 116.9  | 0.25   | 31.9   | 10.5  | 571.8  | 30.3    | 0.61        |
| 50        | 140.10   | 5.27       | 0.481 | 10.60   | 488     | 57.4    | 118.9  | 0.26   | 32.9   | 10.4  | 571.8  | 30.5    | 0.61        |
| 55        | 144.50   | 5.57       | 0.469 | 10.36   | 486     | 56.7    | 121.1  | 0.24   | 31.4   | 9.9   | 567.3  | 29.8    |             |
| 63        | 179.30   | 5.60       | 0.480 | 10.78   | 490     | 58.3    | 128.1  | 0.23   | 33.6   | 10.8  | 571.8  | 30.6    |             |
| 82        | 221.00   | 6.42       | 0.501 | 10.65   | 491     | 58.6    | 135.1  | 0.26   | 35.6   | 10.2  | 571.5  | 30.8    | 0.62        |
| 92        | 6.58     | 0.485      | 10.46 | 489     | 58.6    | 136.0   | 0.22   | 36.7   | 10.3  | 575.9  | 30.8    | 0.60        |
| 107       | 324.00   | 7.99       | 0.516 | 10.98   | 490     | 58.9    | 142.8  | 0.35   | 37.6   | 10.1  | 573.1  | 30.9    | 0.66        |
| 122       | 290.30   | 7.58       | 0.523 | 10.85   | 492     | 59.5    | 147.9  | 0.24   | 38.7   | 10.1  | 561.7  | 30.6    | 0.62        |
| 127       | 268.50   | 7.52       | 0.509 | 10.70   | 488     | 58.2    | 149.3  | 0.23   | 37.2   | 9.6   | 567.6  | 30.6    |             |
| 134       | 277.90   | 8.03       | 0.531 | 10.88   | 491     | 59.3    | 151.1  | 0.23   | 40.2   | 9.9   | 573.3  | 31.2    | 0.65        |
| 142       | 293.00   | 8.33       | 0.532 | 10.99   | 489     | 59.1    | 153.7  | 0.23   | 41.0   | 9.9   | 572.3  | 30.8    | 0.64        |
| 153a      | 6.94     | 3.00       | 0.422 | 10.54   | 483     | 53.7    | 89.9   | 0.17   | 26.7   | 9.8   | 560.8  | 28.8    |             |
| 162a      | 40.13    | 3.99       | 0.473 | 10.84   | 485     | 55.7    | 100.6  | 0.20   | 29.7   | 10.5  | 564.8  | 29.7    | 0.59        |

Note. Core location: 37°58.049′N; 26°5.489′W; gray areas indicate ash and tephra layers.

aSamples were contaminated with seawater.
$^{44}\text{Ca}/^{42}\text{Ca}$ from that of the international Ca standard NIST SRM 915a in per mil (‰). Long-term $\delta^{44}/^{42}\text{Ca}$ of the reference materials NIST SRM 915b (0.35 ± 0.11‰, 2 SD, $n = 13$), NIST SRM 1486 (−0.50 ± 0.05‰, 2 SD, $n = 131$) and IAPSO (0.89 ± 0.06‰, 2 SD, $n = 128$) agree well with the literature values. A procedural blank for the Ca isotope work was determined and found to contribute less than 1% of the processed Ca.

### 2.9. Mg Isotopes

Mg was separated from matrix elements by cation chromatography using DOWEX AG 50 W-X12 in polypropylene columns. Mg was eluted using HNO₃ (2 N). Splits (1 ml) before and after the Mg elution peak were screened for Mg as indicator for quantitative ion separation.

Mg isotope ratios were analyzed on a Neptune Plus MC-ICP-MS at Bundesanstalt für Materialforschung, Berlin. Samples and standards were introduced into a SIS spraychamber using a PFA microflow nebulizer with an uptake rate of 165 μl/min. Measurements were done in medium resolution mode using a normal sample cone and a X-skimmer cone. Procedural blanks are typically <7 ng Mg, of which <2 ng derived from the column procedure.

Measured Mg isotope ratios were normalized to the standard ERM-AE 144 (Vogl et al., 2016) to compensate for mass bias drift (i.e., SSB). Samples and standard were diluted in HNO₃ (0.32 M) to ≈ 0.75 μg/mL Mg, where matching was better than 12%. Isotope ratios are reported in the $\delta$ notation, that is, as the deviation of a measured isotope intensity ratio ($I$) with the high mass isotopes $^{25}\text{Mg}$ or $^{26}\text{Mg}$ over the low mass-isotope $^{24}\text{Mg}$ of a sample (smp) from that of a standard (std):

$$
\delta M_{24}^{x/z} = \frac{\left( \frac{I(^{25}\text{Mg})}{I(^{24}\text{Mg})} \right)_{\text{smp}} - \left( \frac{I(^{25}\text{Mg})}{I(^{24}\text{Mg})} \right)_{\text{std}}}{\left( \frac{I(^{25}\text{Mg})}{I(^{24}\text{Mg})} \right)_{\text{std}}} \times 1000
$$

(1)

$\delta$ values (abbreviated as $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$) were converted from the ERM-AE144 reference frame into the DSM3 reference frame using equation (Vogl & Pritzkow, 2010) for $\delta$ values obtained from the above equation in their basic form (no %, ppm, or else). When $\delta$ values in % are to be used, they have to be divided by 1,000 before entering into the following equation.

$$
\delta^{x/z}E(\text{spl})_{\text{std A}} = \delta^{x/z}E(\text{spl})_{\text{std A}} - \delta^{x/z}E(\text{std B})_{\text{std A}} + \left( \delta^{x/z}E(\text{spl})_{\text{std A}} - \delta^{x/z}E(\text{std B})_{\text{std A}} \right)
$$

(2)

As quality control standards we have analyzed NASS-6 (North Atlantic Seawater, NRC Canada) and the reference material ERM-AE145. NASS-6 yields $\delta^{25}\text{Mg}_{\text{DSM3}} = -0.37 ± 0.04$%, and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.74 ± 0.06$% (2 SD, $n = 4$), identical within 2 SD to the published values of NASS-6 by Wombacher et al. (2009) with $\delta^{25}\text{Mg}_{\text{DSM3}} = -0.43 ± 0.07$% (2 SD, $n = 8$) and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84 ± 0.16$% (2 SD, $n = 4$). Our measurements of ERM-AE145 yield $\delta^{25}\text{Mg}_{\text{DSM3}} = -2.30 ± 0.05$% and $\delta^{26}\text{Mg}_{\text{DSM3}} = -4.58 ± 0.08$% (2 SD, $n = 3$), identical within 2 SD with published values in Vogl et al. (2016) with $\delta^{25}\text{Mg}_{\text{DSM3}} = -2.30$% and $\delta^{26}\text{Mg}_{\text{DSM3}} = -4.61$%.

The uncertainty of $\delta$-values for the entire dissolution, separation and measurement procedure is estimated to <0.1‰ (2 SD).

### 2.10. Head Space Gas Analyses

Headspace gas composition of 20-ml glass vials containing 3 cm³ of sampled sediment and additional 6-ml NaCl-solution were prepared according to Sommer et al. (2009). The vials were stored upside down at room temperature until measurement by using gas chromatography at GEOMAR. One hundred microliters of headspace gas was injected into a Shimadzu gas chromatograph (GC-2014), equipped with flame ionization detector and thermal conductivity detector (carrier gas: He 5.0; HayeSepTM Q 80/100 column, column length: 2 m; column diameter: 1/8”). The detection limits for CH₄ and CO₂ were 0.1 ppmV and 100 ppmV, respectively. Precision was about 4 % (2 SD).
Porewater concentrations of dissolved methane (mmol per liter porewater) were calculated by considering measured sediment porosity, molar volumes at laboratory pressure, and temperature. CO₂ values were used to determine pH values using the co2sys.xls program by Pelletier et al. (2005).

2.11. Endmember Calculations

Endmember (EM) calculations were performed for Mg, Ca, SO₄, and Sr, assuming binary mixing of seawater and the theoretical fluid EM. To calculate fluid EM we used element ratios versus elements for ⁸⁷Sr/⁸⁶Sr versus Sr, Mg/Sr versus Mg, Mg/Ca; Ca, and Mg/SO₄ versus SO₄. Seawater values were used as follows: ⁸⁷Sr/⁸⁶Sr = 0.709176, Sr = 90 μM, SO₄ = 27.8 mM, Ca = 10 mM, and Mg = 53.2 mM. For the fluid EM, a fixed value is required, which is typically Mg = 0 for hydrothermal fluids. Since this is not possible in this case we approximate EM concentrations by using a fixed ⁸⁷Sr/⁸⁶Sr ratio (see details in section 4.6). For each element ratio versus element concentration we calculated a mixing line using the following equation (here shown for the example ⁸⁷Sr/⁸⁶Sr vs. Sr):

\[
\frac{\text{Sr}_{b}}{\text{Sr}_{a}} = \frac{f_b [\text{Sr}]_b + (1-f_b) [\text{Sr}]_a}{f_b [\text{Sr}]_b + (1-f_b) [\text{Sr}]_a}
\]

A comprehensive list for all used element ratios with all data can be found in the supporting information.

2.12. Thermodynamic Model

The saturation state (SI) of caminite was calculated by comparing the ion activity product (IAP) of the solubility reaction to the corresponding thermodynamic equilibrium constant (K):

\[
SI = \log \left( \frac{\text{IAP}}{K} \right)
\]

The following stoichiometry was adopted for the dissolution reaction (Janecky & Seyfried, 1983):

\[
\text{MgSO}_4 0.25\text{Mg(OH)}_2 0.2 \text{H}_2\text{O} + 0.8 \text{H}^+ \leftrightarrow 1.25 \text{Mg}^{2+} + \text{SO}_4^+ + \text{H}_2\text{O}
\]

So that the equilibrium constant is defined as

\[
K_{\text{caminite}} = \frac{a_{\text{Mg}} a_{\text{SO}_4}}{(10^{-\text{pH}})^{0.8} a_{\text{H}_2\text{O}}}
\]

where a represents the species activities.

To test the evolution of the saturation index over a broad temperature and pressure range, three different thermodynamic equilibrium constants (valid for a SO₄/Mg ratio of 0.625) were chosen from the work by Janecky and Seyfried (1983). In the lower temperature region \(K_{\text{caminite}}\) equals 5.3 and is valid for 25 °C and 1 bar. For data points near 200 °C \(K_{\text{caminite}}\) is assumed to be −1.98 and is valid for 200 °C and 500 bar and the SI for 300 °C uses the value −5.59 for the equilibrium constant and is valid for 300 °C and 500 bar.

Species activities were calculated based on the molal concentration (m) and the activity coefficient (\(\gamma\)):

\[
a = \gamma m
\]

The activity coefficients and the activity of water were computed based on the Pitzer model as described in and originally derived by Pitzer and Mayorga (1973). Interactions among the major sea ions were considered including Na, Mg, Ca, K, Cl, and SO₄ and their concentrations were set either to the bottom water values or the extrapolated endmember values. Respective Pitzer parameters were derived from internally consistent collections (Greenberg & Moller, 1989; Pabalan & Pitzer, 1987), which incorporate the effects of in pairing into their parameterization. It should be noted that the temperature range for the Pitzer data applied in the calculation of the species activities in most cases does not exceed 200 °C. Instead of extrapolating the
Pitzer parameters outside the stated temperature range, we use the parameterization of the upper temperature limit. For comparison, caminite SI is calculated for a range of pH values (7, 7.5, and 8). Also, while the equilibrium constants for elevated temperatures are valid only for 500 bar, we have also included the SI values that were calculated with activities for 1 bar to allow for a rough estimate of the pressure effect on the SI.

2.13. Transport Model

A simple 1-D transport model including diffusion and advection was applied using Mathematica 11.3 (Wolfram Research, 2018). The model was solved for the solute species Mg, Ca, TA, and SO4. The general differential equation reads as follows:

$$\frac{\partial \phi \cdot C}{\partial t} = \frac{\partial (\phi \cdot D_s \cdot \frac{\partial C}{\partial x})}{\partial x} - \frac{\partial (\phi \cdot v \cdot C)}{\partial x}$$  \hspace{1cm} (7)

where $t$ is the time (yr), $x$ is the depth (cm), $\phi$ is the porosity (unitless), $C$ is the concentration of solutes (mmol dm$^{-3}$), $D_s$ is the diffusion coefficient in the sediments (cm$^2$ yr$^{-1}$) corrected for tortuosity after (Boudreau, 1997), and $v$ is the fluid velocity (cm yr$^{-1}$). The model did not include any reactions. Initial porosity was set to 0.8, and porosity after compaction was set to 0.6 to fit the measured profile. Boundary conditions were defined for the sediment surface (0 cm) with ambient seawater concentrations (Mg = 54 mM, Ca = 10.2 mM, SO$_4$ = 28.7 mM, and TA = 2.7 meq/L), and for 300-cm depth (Mg = 63 mM, Ca = 11.5 mM, SO$_4$ = 33 mM, and TA = 11 meq/L; note that the lower boundary conditions are not equal to the calculated EM). The model was run into steady state. The upward flow velocity was determined by fitting the model to the measured pore water data.

2.14. Seismic Data

The reflection seismic data (Figure 1c) have been collected during RV Meteor expedition M79/2 (Hübscher, 2012). Four so-called GI-Guns created the seismic signal and a 144-channel, 600 m-long seismic streamer, with a channel spacing of 4.2 m, recorded the data. Processing included band-pass filtering, energy balancing, NMO-correction, stacking, time-migration, and fx-deconvolution. For an overview of the marine seismic method, see Hübscher and Gohl (2014).
3. Results

3.1. Pore Fluid Composition and Isotope Data

Pore fluid depth profiles for TA, Mg, Ca, SO₄, Li, and Sr are shown in Figures 2a–2f, and data are provided in Tables 1 (GC50) and 2 (GC51). The reference core GC50 shows a slightly elevated TA with 3.84 meq/L at 133 cm below seafloor (bsf). Ca is slightly decreasing from 10.86 at 12 cm bsf to 9.72 mM at 118 cm bsf. Sr is depleted in with respect to ambient bottom water (91 μM), with a decrease to 86.73 μM at 133 cm bsf. Mg, SO₄, and Li do not show any deviations from seawater values. For GC51, TA increases downcore from seawater values of 2.35 meq/L to up to 8.33 meq/L at 142 cm bsf. Also Mg is increasing with depth to 59.46 mM at 122 cm bsf, and SO₄ increases from 27.8 to 31.21 mM at 134 cm bsf. Ca remains almost constant over depth, with a slight increase up to 10.99 mM at 142 cm bsf with respect to seawater (10.2 mM). Sr in GC51 increases up to 150 μM at 142 cm bsf. In addition to that Li is also increasing to 40 μM in GC 51.

Isotope systematics of GC51 show a strong deviation from seawater for $^{87}$Sr/$^{86}$Sr and $^{34}$S, $^{18}$O$\text{SO}_4$, $^{26}$Mg, and $^{30}$Si (Figure 4 and Table 3). $^{87}$Sr/$^{86}$Sr shows a decreasing trend from 0.7091 (present-day seawater) to 0.7074 at 142 cm bsf. $^{26}$Mg$_\text{GC51}$ values of the sampled fluids show an increase in $^{36}$Mg from −0.81‰ (seawater) to −0.18‰ at 142 cm bsf. $^{34}$S$_\text{GC51}$ increases with depth from 21.9‰ at 16 cm bsf to 24.7‰ at 134 cm bsf. $^{30}$Si$_\text{GC51}$ does decrease slightly from 0.84‰ at 50 cm bsf to 0.77‰ at 142 cm bsf. $^{36}$Si$_\text{GC51}$ shows an increase in $^{30}$Si from seawater values of 52.6 ppm in GC51. The calculated pH values from fCO$_2$ and TA concentrations are for both cores remaining at background values with slightly elevated values for GC51. fCO$_2$ values go up to 5,599 μatm at 166 cm bsf. Also Mg is increasing to 40 μM in GC 51.

3.2. Solid Phase

The sediments largely consist of nannofossil-rich mud to mud-rich nannofossil ooze with variable admixture of fresh volcanic, silicilastic, and biogenic material. A detailed description of sediments and components can be found in the supporting information. Organic input to sediments is low resulting in an average amount <0.3% of CaCO$_3$ proportion of the sediments is in average ~20%. The main composition of the sediments is rather constant over depth and does not show pronounced differences between the two coring locations (Figures 2g–2l). The Chemical Index of Alteration (CIA; Nesbitt & Young, 1982) is used as a measure to determine the degree of weathering of the sediments. The CIA is calculated as follows: CIA = Al$_2$O$_3$/ (Al$_2$O$_3$ + CaO$^+$ + Na$_2$O + K$_2$O) × 100. CaO$^+$ is the Ca bound to silicates and is determined by subtracting Ca bound to carbonates (CaCO$_3$ = 8.33 × TIC) from total Ca. The average CIA for both cores is between 40% and 60% (details can be found in the supporting information data).

3.3. Head Space Gas

Head space gas analyses for CH$_4$ and CO$_2$ did not show any variations with depth (see supporting information data). CH$_4$ values stay at background values. The highest methane concentration was observed in GC50 at 166 cm bsf with 0.739 μM. In addition to that, also fCO$_2$ values remain at background values with slightly elevated values for GC51. fCO$_2$ values go up to 5,599 ppm in GC51. The calculated pH values from fCO$_2$ and TA concentrations are for both cores about 7.5.

4. Discussion

In the following, we will present a comprehensive analysis of potential processes that might explain the unusual geochemical pore fluid signature of GC51 with anomalously high TA, Mg, and SO$_4$ concentrations.

4.1. Near-Surface Diagenetic Processes

Pore water profiles of enriched species display a slight exponential curvature within the uppermost ~50 cm (Figure 2). Generally, such type of profiles can either be the result of continuous reactive processes or be caused by fluid advection. Reactions typically include organic matter
degradation, secondary redox reactions, weathering/alteration of rocks, and mineral dissolution reactions. Our data suggest that the reactive influence in the shallow sediments is only minor: The TR in the Central North Atlantic Ocean receives only minor input of organic matter reflected by very low concentrations of TOC (<0.3 wt.%). Moreover, the increase in TA that results from organic matter degradation should also have been observed in GC50 where the increase is almost negligible. The increase in TA could also be explained by the anaerobic oxidation of methane (AOM) coupled to sulfate reduction. This would require a deep methane source, but neither indications for sulfate reduction (SO₄ concentrations are elevated in GC51) nor methane enrichment were detected in GC51. We assume that some of the elevated TA in GC51 comes from minor organic matter degradation, but additional processes have to be considered. Weathering/alteration of rocks or mineral dissolution processes could on first sight explain the curvature in the increasing profiles in GC51. Weathering of the volcanioclastic sediments can have an effect on the fluid composition, as minerals like Mg-smectite and zeolites can be formed or elements can be released due to volcanic glass dissolution (Schacht et al., 2008). However, visual analyses of the surface sediments by smear slides did not reveal indications for altered volcanic compounds or any secondary Mg or SO₄ bearing minerals (e.g., being indicative for hydrothermal alteration). Furthermore, the sediments of the reference core GC50 are identical in composition and depth of stratigraphic layers compared to GC51 (Figures 2g–2l). Intense weathering and formation of secondary minerals typically results in the loss of alkaline and alkaline earth metals, which is reflected in high values (>75%) of the CIA. CIA values for both cores do not show any evidence for pronounced alteration processes and no depth-related trends.

4.2. Indications for Upward Fluid Flow
The lack of evidence for alteration processes in the near-surface sediments suggests that the geochemical composition of the fluid is not the result of in situ processes but instead seems to be derived from deeper sources. The application of a simple numerical fluid transport model was carried out to test if the shape of the profiles (Figures 2a–2l) can be explained by an advective flux component. We tested two model scenarios (i) only diffusion and (ii) advection and diffusion (Figure 3). Indeed, a reasonably good fit to the data could be obtained with a fluid velocity of 0.5 cm yr⁻¹, emphasizing the need to include the advection process in the profile interpretation. With shallow diagenetic processes being only of minor importance, the hypothesis that fluids are derived from a deeper source is supported.

4.3. Hydrothermal Signature
With respect to the location close to an active spreading center and recent magmatic activity in the area, we suspect that the observed pore water anomalies are related to hydrothermal activity. Many processes in hydrothermal systems affect Mg and SO₄ concentrations of fluids. Below, we analyze potential processes that might cause such anomalies and discuss their likeliness.

4.3.1. SO₂-Enriched Volatiles
Hydrothermal fluids enriched in Mg and SO₄ have been reported from other regions, for example, the DESMOS caldera (Gamo et al., 1997; Seewald et al., 2015). In these cases, the excess SO₄ concentrations were explained by the discharge of SO₂-enriched magmatic volatiles and their subsequent disproportionation to SO₄. Such highly acidic fluids can leach Mg-rich silicate minerals from the host rock, resulting in increased Mg concentrations (Gamo et al., 1997). Sulfur of magmatic origin can be distinguished from seawater sulfur and other sources by its δ³⁴S signature. Fluids sampled at the DESMOS caldera show much lower values compared to seawater and, hence, are typical for a mantle sulfur source (δ³⁴S_Mantle < 5‰; Seewald et al., 2015). In contrast, δ³⁴S_GC51 values increase slightly and stay at levels above seawater (Figure 4a). A mantle origin of SO₄ via disproportionation from SO₂ we can rule out.

4.3.2. Anhydrite Dissolution
One of the most abundant minerals formed in hydrothermal systems is anhydrite. Hydrothermal anhydrite formation is a major sink for SO₄, resulting in the removal of SO₄ from fluids (Alt, 1995). The mineral phase forms at temperatures above 150 °C but is generally not present in old, altered oceanic crust as it dissolves at lower temperatures (Alt, 1995). Dissolution of anhydrite could therefore be a source for SO₄ to the pore fluids (Gieskes et al., 2002). δ³⁴S values of anhydrite are typically around or slightly above seawater (Alt, 1995), matching our observations in the fluids (Figure 4a). In contrast, Ca concentrations are not significantly elevated in GC51, albeit the fact that anhydrite dissolution releases equal amounts of Ca and SO₄ to the pore fluids. Moreover, an extensive dissolution of anhydrite should result in much stronger deviations of the
δ⁴⁴/⁴²Ca_GC51 = 0.77‰ from δ⁴⁴/⁴²Ca_seawater = 0.89‰ (Figure 4b). Anhydrite has a shift of 0.5‰ from seawater to lower values (Amini et al., 2008). Thus, an additional sink for Ca, for example, calcium carbonate formation or ion exchange with clay minerals would be required or only a minor dissolution of anhydrite seems plausible here. Additionally, dissolution of anhydrite could explain the elevated Sr concentrations. Sr is an abundant trace element in hydrothermally formed anhydrite (Teagle et al., 1998). However, anhydrite dissolution cannot explain the increased TA or Mg concentration.

4.3.3. Mg-Rich Smectite

Mg-rich smectite, such as saponite, is the major sink for Mg in hydrothermal systems (Alt et al., 1986). In contrast to anhydrite, saponite is present in aged oceanic crust and is not dissolving during cooling of hydrothermal systems (Alt & Honnorez, 1984). Mg Smectite dissolution can be excluded as potential source for the Mg excess relative to seawater. Clay minerals do have a significant ion exchange capacity due to their large surface area. The main cations being exchanged are Mg, Ca, H, and Na (Wimpenny et al., 2014). Accordingly, smectite could be a potential sink for Ca and source for Mg. The overall δ²⁶Mg of Mg-smectites is above 0‰ (Figure 4c, Teng, 2017). Most of Mg is bound to the clay mineral lattice and only absorbed Mg in the interlayers can be exchanged. The exchangeable Mg of smectite is typically around −1.5‰ δ²⁶Mg (Wimpenny et al., 2014) and therefore lower than seawater values. Consequently, ion exchange should result in a decrease of the δ²⁶Mg value in the fluid relative to the δ²⁶Mg in seawater, which is opposite to the δ²⁶Mg values in GC51. In contrast, the dissolution of Mg-rich silicates by acidic fluids yields δ²⁶Mg values between −0.15‰ and −0.25‰ δ²⁶Mg (Teng, 2017), identical with the pore fluid δ²⁶Mg in GC51.

Silicon isotopes (δ³⁰Si) can be used as an additional fluid tracer, as different reservoirs are characterized by distinct δ³⁰Si values. Mantle fluids have an average δ³⁰Si value of −0.3‰ (De La Rocha et al., 2000). Also secondary clay mineral dissolution would enrich the fluid phase in light ³⁰Si, as clays show on average low δ³⁰Si values of −2.1‰ (De La Rocha et al., 2000; Ziegler et al., 2005; Opfergelt et al., 2010). The δ³⁰Si values in GC51 range between +1.2‰ and +1.8‰ (Figure 4d) and thus overlap within error of the Si isotope value of the deep Atlantic water at 2,800 m water depth (average δ³⁰Si_Atlantic = +1.6‰ (Brzezinski & Jones, 2015; De Souza et al., 2012), and the reference core GC50, which has an average δ³⁰Si value of +1.5‰ (see Table 3). Consequently, dissolution of secondary Si-rich minerals or mixing with mantle fluids can be excluded as well.

4.3.4. Low-Temperature Weathering of Peridotite

Snow and Dick (1996) proposed that the weathering of peridotite at temperatures below 150 °C results in the pervasive loss of Mg of the basement. Slow-spreading ridges are the typical environments were peridotites get exposed to the seafloor surface. Ligi et al. (2013) proposed that the increase in number of slow-spreading ridges in the past 80 Ma have contributed to a shift in the global Mg cycle as enhanced weathering of peridotites could have occurred. However, up to date no Mg-rich fluids have been found in slow-
spreading environments. The hyperslow spreading TR could be suitable for the conditions defined for high Mg vents by Ligi et al. (2013). The crustal thickness of the basaltic Azores Plateau is about 14 km (Escartin et al., 2001), and exposure of mantle peridotite is unlikely here. In addition to that, no description of exposed peridotites is available for the TR. Nevertheless, if a deep fluid circulation could reach peridotites, low temperature weathering of peridotites results in the formation of Mg‐smectite, accompanied with a fractionation of Mg isotopes (Liu et al., 2017). According to the authors fluids enriched in Mg affected by low‐temperature weathering result in $\delta^{26}\text{Mg}$ values lower than seawater by $-1.31$‰, while $\delta^{26}\text{Mg}$ values in core GC51 are enriched with respect to seawater. Hence, we conclude that this process is not or at least not significantly affecting the fluid composition at GC51.

4.4. Dissolution of Caminite

None of the processes described above can satisfactorily explain the geochemical pore fluid anomalies of high Mg, SO$_4$, and TA concentrations observed in GC51. All of the above described processes only impact one of the three enriched species. A complex succession of these processes can also not satisfactorily explain the fluid geochemistry at GC51. We suggest therefore that we see here as of yet underestimated case where the dissolution of the hydrothermally formed mineral caminite may offer an explanation for the observed pore fluid deviations. Caminite is a magnesium‐sulfate‐hydroxide‐hydrate (MgSO$_4$ 0.25 Mg(OH)$_2$ 0.2H$_2$O), which to date has been only found once in a natural environment. Haymon and Kastner (1986) reported caminite from a black smoker site on the East Pacific Rise 21°N, precipitating directly from heated seawater. Furthermore, this mineral has been synthesized under laboratory conditions (Janecky & Seyfried, 1983). Both studies indicate that high fluid temperatures of >240 °C are needed to form caminite. Although caminite can be regarded as a rare mineral, Haymon and Kastner (1986) proposed that it could be an abundant mineral in hydrothermal recharge zones where high temperatures are present in the system while Mg smectite formation is largely inhibited. The authors assumed that such a scenario is possible in hydrothermal systems with little fresh basaltic glass present in the recharge zone. Both studies indicate that high fluid temperatures of >240 °C are needed to form caminite. Although caminite can be regarded as a rare mineral, Haymon and Kastner (1986) proposed that it could be an abundant mineral in hydrothermal recharge zones where high temperatures are present in the system while Mg smectite formation is largely inhibited. The authors assumed that such a scenario is possible in hydrothermal systems with little fresh basaltic glass present in the recharge zone. This implies that during a former hydrothermal alteration Mg‐smectite already formed and the reactivity of the basement is lower compared to young oceanic basement. The basement of the Azores Plateau has undergone intensive alteration (Beier et al., 2019); hence, there is the possibility that smectite formation has occurred before and no fresh basaltic glass is present at this location in the basement. Moreover, an enrichment of Li in fluids is indicative for elevated fluid temperatures in the subsurface (e.g., Scholz et al., 2010). The Li concentrations in GC51 are slightly elevated compared to the reference core; we can therefore assume that high fluid temperatures are present in the subsurface in the TR. Thus, the general conditions for the formation of caminite (as defined by Haymon & Kastner, 1986) are likely to be met in the TR. It has also been shown that caminite dissolves rapidly at temperatures <240 °C
of Sr, Mg, Ca, and SO4 are coherent as the and a workaround had to be found to constrain the unknown accordingly (e.g., Douville et al., 2002). However, the high Mg concentrations complicate the problem, general performed using a 0

Mg, Ca, and SO4 are coherent and Sr can therefore be used as a tracer for EM calculation.

Concentrations of Sr, Mg, Ca, and SO4 are coherent as they have different concentration levels in the pore waters sampled in GC51 are a mixture of ambient pore water (seawater) and the deep fluid. EM calculations are used to determine maximum concentrations of the fluid source. For hydrothermal fluids this is in general performed using a 0-mM EM for Mg and calculate respective element enrichments or depletions accordingly (e.g., Douville et al., 2002). However, the high Mg concentrations complicate the problem, and a workaround had to be found to constrain the unknown fluid endmember at depth. The concentrations of Sr, Mg, Ca, and SO4 are coherent as the fluid mixture (from caminite and to a lower extent anhydrite dissolution) is generated in the same region and transported to the seafloor. Caminite redissolution can explain the increase of Mg, SO4, and TA in pore water of GC51, but elevated Sr concentrations remain a puzzling observation. In laboratory experiments caminite did not incorporate Sr into the mineral structure (Janecky & Seyfried, 1983). The absence of Sr in caminite thus indicates that the enrichment of Sr in pore fluids cannot be explained by caminite dissolution. Notably though, caminite is typically associated with anhydrite (Haymon & Kastner, 1986), which incorporates Sr and other divalent ions (Teagle et al., 1998). As discussed before, an accompanied minor dissolution of anhydrite could explain the Sr increase. Also, a small increase in Sr from anhydrite dissolution would have a minor affect SO4 and Ca concentrations, as they have different concentration levels in the pore fluid. Thus, the suggested fluid mixture is generated by different sources but in the same depth and transported to the seafloor. Concentrations of Sr, Mg, Ca, and SO4 are coherent and Sr can therefore be used as a tracer for EM calculation.

4.5. Endmember Calculation

The fluids sampled in GC51 are a mixture of ambient pore water (seawater) and the deep fluid. EM calculations are used to determine maximum concentrations of the fluid source. For hydrothermal fluids this is in general performed using a 0-mM EM for Mg and calculate respective element enrichments or depletions accordingly (e.g., Douville et al., 2002). However, the high Mg concentrations complicate the problem, and a workaround had to be found to constrain the unknown fluid endmember at depth. The concentrations of Sr, Mg, Ca, and SO4 are coherent as the fluid mixture (from caminite and to a lower extent anhydrite dissolution) is generated in the same region and transported to the seafloor. We chose to base our estimates on 87Sr/86Sr ratios. Sr isotopes and concentration (1/Sr) plot on a linear regression line. The minimum isotope ratio can be approached for 1/Sr approaching toward 0, resulting in an 87Sr/86Sr of 0.7049 for GC51 (Figure 5c). Interestingly, this value is in agreement with ratios of the oceanic basement in the TR (0.7035 to 0.7060; Beier et al., 2008; White et al., 1976). Sr isotopic ratios in the west are lower and shifting to higher ratios to the east. The sample location of GC51 is located in the part of the TR where values for 87Sr/86Sr are around 0.705. Moreover, the proposed EM value represents also Sr isotope ratios of hydrothermally formed anhydrite (Teagle et al., 1998). Assuming Sr release is caused by minor anhydrite dissolution as discussed before, this Sr release can also cause the Sr isotope deviation. Therefore, we take 87Sr/86Sr = 0.7049 as a fixed EM for the following EM calculation of the other elements. The EM calculation was then performed as described in section 2.11 assuming a binary mixing of seawater and the EM. The best fit for 87Sr/86Sr versus Sr could be obtained with a Sr concentration of 650 μM. On a mixing line between seawater (87Sr/86Sr = 0.709176; Sr = 91 μM) and fluid EM (87Sr/86Sr = 0.7049; Sr = 650 μM) the measured sample lies at 10% EM fluid (Figure 5c). Accordingly, we used in a next step the Sr concentration as a fixed value and deduced the Mg concentration using the Sr/Mg ratio. The same approach was used to deduce EM Ca and SO4...
concentrations. The resulting EMs are as follows: Mg = 85 mM, SO₄ = 47 mM, Sr = 650 μM, Ca = 12 = mM, and ⁸⁷Sr/⁸⁶Sr = 0.7049 (Figure 5). Nevertheless, this method is based on a number of assumptions (e.g., no modification of fluids in the sediment column), which cannot be further constrained, and hence, the EM calculation can only be regarded as a rough approximation.

Finally, we apply thermodynamic calculations to test the plausibility of the proposed scenario. The caminite saturation index—based on Pitzer-derived activities (Pitzer & Mayorga, 1973)—is calculated for seawater and the theoretical EM concentrations. The results in Figure 6 show that seawater and EM are strongly undersaturated in the low-temperature region and that both solutions are around the state of saturation at temperatures around 200 °C. Temperatures above 200 °C likely induce strong oversaturation. The similarity in SI values for seawater and EM stems from the fact that while SO₄ and Mg concentrations increase in EM solutions, their activity coefficient decreases compared to seawater. Variations in pH between 7 and 8 do not significantly influence the SI region for a given temperature and do not influence the overall interpretation. The good agreement between the calculated fluid EM and caminite solubility at elevated temperatures supports the theory that caminite controls the fluid composition at depth. Taking everything together, caminite dissolution offers the most plausible explanation for the seen fluid deviations in GC51.

4.6. Implications

The presence of caminite confirms the existence of a deep submarine hydrothermal system in the TR, which has not been reported yet in this region. Listric faults offer suitable fluid pathways, and advective fluxes, albeit low (0.5 cm/yr), imply an ongoing fluid circulation in the basement. Dissolution of caminite occurs when temperatures in hydrothermal systems drop below 240 °C. Our conclusion is that the system is currently in a waning state. Our conceptual model (Figure 7a) is based on the idea that a magma intrusion in the basement below the volcanic cone is currently cooling and the isotherms are retracting. Fluids circulating through the basement may dissolve caminite at temperatures <240 °C, but temperatures are still high enough to drive active fluid convection. Fluids affected by caminite dissolution are transported along the listric faults via diffusion and slow advection through the sediments to the surface (Figure 7b). The fact that caminite starts to dissolve rapidly when temperatures drop might explain why it has been rarely reported to date. Our findings support the hypothesis by Haymon and Kastner (1986) that caminite can be abundant under specific conditions in hydrothermal recharge zones. To date, only for one further vent, at Brother lower cone (Kermadec arc, SW Pacific), caminite dissolution has been hypothesized to play a role in fluid generation (Kleint et al., 2019). Numerous
hydrothermal vents exist in slow-spreading settings, for example, Southwest Indian Ridge (German et al., 1998), but for none of them high Mg/SO₄ fluids have been reported. However, crustal age and geological setting would be favorable to host this type of vents. For the TR, 251 magmatic intrusions and submarine volcanoes in aged oceanic crust have been reported (Weiß et al., 2015), providing potentially suitable conditions for a widespread formation and dissolution of caminite.

5. Summary and Conclusions

We present pore fluid data from a gravity core taken at the rim of a submarine lava flow in the TR, which are characterized by high Mg, SO₄, and total alkalinity concentrations. By applying comprehensive isotope measurements and numerical modeling, we could exclude several known diagenetic and hydrothermal processes to cause the observed deviations. The most straightforward explanation for our findings is the dissolution of hydrothermally formed caminite. The literature offers little information on caminite, but it has been proposed that it can precipitate under specific conditions in hydrothermal recharge zones, which are generally met in the TR. Thus, our findings support the hypothesis by Haymon and Kastner (1986) suggesting that caminite occurrence could be more common than previously thought, especially in active hydrothermal systems before subsiding temperatures induce rapid caminite dissolution. This hydrothermal signal is the first indication of a deep submarine hydrothermal system in the TR. Hydrothermal systems are important sinks for Mg in the global budget (Mottl & Wheat, 1994). A widespread dissolution of caminite in cooling hydrothermal systems might cause a nonnegligible flux of Mg to the ocean. The additional strong fractionation measured for δ²⁶Mg isotopes implies neglected effects on the oceanic Mg budget and seawater δ²⁶Mg.

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