Barium isotopes in mid-ocean ridge hydrothermal vent fluids: a source of isotopically heavy Ba to the ocean

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Highlights:

1. MOR vent fluids show the largest range of $\delta^{138/134}$Ba seen so far in marine systems.

2. Endmember vent fluid $\delta^{138/134}$Ba values are the same as those of the source rocks.

3. Barite precipitation leads to high $\delta^{138/134}$Ba values in vent fluids as they evolve.

4. Hydrothermal Ba input may explain non-conservative $\delta^{138/134}$Ba seen in deep waters.

5. Hydrothermal input contributes 3-9% of the Ba in some Atlantic deep waters.

Abstract

      Mid-ocean ridge (MOR) hydrothermal vent fluids are enriched with dissolved barium, but due to barite ($BaSO_4$) precipitation during mixing between Ba-bearing vent fluids and SO_4-bearing seawater, the magnitude of hydrothermal Ba input to the ocean remains uncertain. Deep-ocean Ba isotopes show evidence for non-conservative behavior, which might be explained by input of isotopically heavy hydrothermal Ba. In this study we present the first Ba isotope data in mid-ocean ridge hydrothermal vent fluids and particles from systems on the Mid-Atlantic Ridge (Rainbow 36°N and TAG 26°N), the East Pacific Rise (EPR9-10°N and 13°N) and the Juan de Fuca Ridge (MEF and ASHES). The vent fluids display a wide range of dissolved Ba concentrations from 0.43 to 97.9 μmol/kg and $\delta^{138/134}Ba$ values from -0.26 to +0.91 ‰, but are modified relative to initial composition due to precipitation of barite. Calculated endmember vent fluid $\delta^{138/134}Ba$ values, prior to barite precipitation, are between -0.17 and +0.09 ‰, consistent with the values observed in oceanic basalts and pelagic sediments. Water-rock interaction at depth in the oceanic crust appears to occur without Ba isotope fractionation. During subsequent venting and mixing with seawater, barite precipitation preferentially removes isotopically light Ba from vent fluids with a fractionation factor of $\Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid}$ = -0.35 ± 0.10 ‰ (2SE, n=2). Based on knowledge of barite saturation and isotope fractionation during precipitation, the effective hydrothermal Ba component that mixes with seawater after barite precipitation has completed can be calculated: $\delta^{138/134}Ba_{hyd}$ = +1.7 ± 0.7 ‰ (2SD). This value is isotopically heavier than deep ocean waters and may explain the observed non-conservative of Ba isotopes in deep waters. These new constraints on hydrothermal Ba compositions enable the hydrothermal input of Ba to Atlantic deep waters to be assessed at ≈ 3 – 9 % of the

50 observed Ba. Barium isotopes might be used as a tracer to reconstruct the history of

51 hydrothermal Ba inputs and seawater SO_4 concentrations in the past.

52

53 **1. Introduction**

54 Mid-ocean ridge (MOR) hydrothermal systems play an important role in

55 determining seawater chemistry (Von Damm, 1990; Elderfield and Schultz, 1996;

56 German and Von Damm, 2003; Tivey, 2007; German and Seyfried, 2014; Humphirs

57 and Klein, 2018; Coogan et al., 2019). Hydrothermal systems are a source of some

58 elements to seawater (e.g. Fe, Mn and Li) and a sink for others (e.g. Mg and SO_4).

59 Hydrothermal vent fluids are enriched in Ba (1 ~ 119 μmol/kg) by up to 1000 times

60 relative to seawater (0.03 ~ 0.2 μmol/kg) (e.g. Butterfield et al., 1994; Charlou et al.,

61 1996; Von Damm et al., 1985; Kumagai et al., 2008; Seyfried et al. 2011).

62 Many processes control the hydrothermal flux of Ba into the ocean. Water-rock

63 interaction releases Ba from source rocks to vent fluids at elevated pressures and

64 temperatures (Von Damm et al., 1985). These source rocks contain Ba at the level of

65 [Ba] = 3.9 – 160.3 ppm in oceanic basalts (Gale et al., 2013) and [Ba] = 350 – 6230

66 ppm in marine sediments (Li and Schoomaker, 2003), explaining the high Ba

67 concentration values in vent fluids. Mixing between these vent fluids and SO_4-bearing

68 seawater, however, leads to barite ($BaSO_4$) precipitation (e.g. Shikazono, 1994; Hanor,

69 2000; Seyfried et al. 2003; Jamieson et al., 2016; Gartman et al., 2019), which removes

70 Ba and reduces hydrothermal Ba input to seawater. Therefore, despite the fact that Ba

71 concentrations in vent fluids are several orders of magnitude higher than in seawater,

72 the 'effective' hydrothermal Ba input to the ocean is smaller and remains uncertain.

73 Barium isotopes have recently been studied as a new tracer to understand the

74 oceanic Ba cycle (Horner et al., 2015; Hsieh and Henderson, 2017; Bates et al., 2017;

75   Bridgestock et al., 2018; Crockford et al., 2019; Cao et al., 2020). In general, seawater

76    $\delta^{138/134}$Ba values range from +0.22 to +0.65 ‰ in the global oceans. The deep Pacific

77   Ocean has higher Ba concentrations (> 0.1 μmol/kg) and lighter $\delta^{138/134}$Ba values (<

78   +0.3‰) than the Atlantic Ocean. The main process controlling observed variations in

79   seawater $\delta^{138/134}$Ba is barite formation and dissolution. This barite precipitation

80   preferentially removes light Ba isotopes from solutions into solid phases (e.g. von

81   Allmen et al., 2010; Böttcher et al., 2018).

82   The Ba isotope composition $\delta^{138/134}$Ba of major inputs and outputs of Ba to the

83   ocean has been assessed. The main input to the ocean is from rivers and is isotopically

84   light, ranging from -0.06 to +0.46 ‰ (Cao et al., 2020; Hsieh and Henderson, 2017;

85   Gou et al., 2020). Estuaries also play an important role in the riverine Ba isotope

86   compositions through adsorption and desorption of Ba between suspended particles and

87   the dissolved phase (Gou et al., 2020). The main output is into marine sediments,

88   particularly as precipitated barite, and is also isotopically lighter than seawater, ranging

89   from -0.21 to +0.11 ‰ in suspended particles and pelagic sediments (Horner et al.,

90   2017; Bridgestock et al., 2018; Crockford et al., 2019). As yet, there are no available

91   data to constrain Ba isotope compositions in marine hydrothermal vent fluids.

92   The degree to which Ba isotopes behave conservatively in the deep ocean is

93   uncertain. Bates et al. (2017) suggested that Ba isotopes in deep ocean waters are mostly

94   conservative during the mixing between North Atlantic Deep Water (NADW, $\delta^{138/134}$Ba

95   ≈ +0.45‰) and Antarctic Bottom Water (AABW, $\delta^{138/134}$Ba ≈ +0.25‰), but Hsieh and

96   Henderson (2017) identified evidence for non-conservative mixing in deep waters, with

97   deviations towards higher $\delta^{138/134}$Ba values than the conservative mixing trend,

98   particularly at depths of 2000 – 3000m (Fig. 1). Hydrothermal Ba inputs may be an

99   explanation for such non-conservative behavior.

100   In this study, we present the first Ba isotope data in hydrothermal vent fluids

101   from 6 hydrothermal systems in both the Atlantic and Pacific Oceans to establish the

102   relationship between vent fluid Ba isotope compositions and hydrothermal processes

103   (e.g. water-rock interaction and barite precipitation). We pair the dissolved and

104   particulate Ba data from the same hydrothermal vent fluids to understand the correlation

105   between barite precipitation and Ba isotope fractionation in hydrothermal systems.

106

107   **2. Materials and methods**

108   **2.1. Hydrothermal vent fluids and particles**

109   All the vent fluid and particle samples analyzed in this study were obtained by

110   the University of Minnesota co-authors over the past 15 years. The fluid samples (21

111   focused-flow and 10 diffuse-flow) were selected from 6 different hydrothermal systems

112   with distinct geologic settings along the mid-ocean ridges in both the Atlantic and

113   Pacific Oceans. Sites included are from the slow-spreading Mid-Atlantic Ridge (MAR):

114   Rainbow (36°N, ultramafic-hosted) and Trans Atlantic Geotraverse (TAG, 26°N, active

115   mound); the fast-spreading East Pacific Rise (EPR): 9-10°N and 13°N (basalt-hosted);

116   the intermediate-spreading Juan de Fuca Ridge (JdFR) in the Northeast Pacific: Main

117   Endeavor Field (MEF) (sediment-influenced) and ASHES vent field, Axial Caldera

118   (ASHES) (Fig. 2). Diffuse-flow samples generally refer to the MOR discharged vent

119   fluids at low temperature (relative to the high temperature focused-flow, > 250°C), low

120   flow rates and broad spatial distributions (Bemis et al., 2012). These fluids have

121   undergone variable mixing with seawater beneath the seafloor prior to venting. In this

122   study, only 3 of the 10 diffuse-flow samples have sufficient Ba for isotope analysis. To

123   assess the controls of Ba isotopes in diffuse-flow vent fluids, more data will be required.

124   Vent fluid samples were collected in a titanium syringe-type gas-tight sampling

125   device (Seewald et al., 2002; Wu et al., 2015). Initial ship-board processing of fluids

126   occurred within hours of sample recovery from the seafloor. In general, subsamples

127   were taken under pressure from each bottle for determination of pH (at 25ºC), H_2S,

128   major dissolved anions and cations, and trace metals. The trace metal aliquot was

129   immediately acidified with high-purity HCl (Optima, Fisher Chemical) to pH ~1. A

130   fraction of this subsample (200 μL) was preserved in pre-weighed and acid-cleaned

131   polyethylene vials before sending to Oxford for analysis of Ba isotopes.

132   Precipitates that formed in the samplers upon cooling and mixing with entrained

133   seawater were rinsed with Milli-Q water, collected on a 0.2 μm nylon filter and

134   subsequently re-dissolved in HCl/HNO_3 (ULTREX, J.T. Baker). These precipitates are

135   commonly called "dregs", and usually contain high levels of transition metals (e.g. Cu,

136   Fe, and Zn). Based on the metal contents, the mineralogy of dregs is mainly sulfides

137   (e.g. chalcopyrite and sphalerite) with other trace metals, such as As, Mo and Ba (Metz

138   and Trefry, 2000; Rouxel et al., 2008; Yucel et al., 2011; Gartman et al., 2014; Gartman

139   et al., 2018). Scanning electron microscopy (SEM) images show that Ba exists as barite,

140   surrounded by sulfides, in the particles precipitated in vent fluids (Gartman et al., 2018).

141   Precipitation of dregs reduces the concentrations or causes isotope fractionation in these

142   elements from the original fluids (Seyfried et al., 2003; Rouxel et al., 2008; James et

143   al., 2014). The amount of metals measured in the dregs was therefore recombined with

144   metals that remained in solution to obtain a complete metal inventory of the vent fluids

145   prior to collection. Dregs are not available for 10 vent fluid samples (out of 31) reported

146   here. These samples are mostly diffuse-flow type with no precipitation of dregs, except

147   for two focused-flow samples (4744-1 and 4744-2) where their dregs were not kept and

had no recorded Ba data. All fluid samples without dregs are reported as uncorrected

data only.

Sample ID (including sample years and submersible dive numbers), vent type,

location, and names are provided in Table 1, as are references to published data and

procedures that provide information critical to the broader interpretation of the Ba data

reported here. Vent fluid chemistries in these and other marine hydrothermal systems

have been well documented (e.g. Campbell et al., 1988; Butterfield et al., 1990; Von

Damm, 1990; Von Damm, 2000; Charlou et al., 2002; Douville et al., 2002; Seyfried

et al. 2003; Seyfried et al., 2011; Fornari et al., 2012). Most of the fluid samples

provided for this study have been analyzed and discussed for other trace elements and

isotopes in previous studies (Foustoukos and Seyfried, 2007; Foustoukos et al., 2009;

Pester et al., 2011; Seyfried et al., 2011; Pester et al., 2014; Syverson et al., 2017;

Scheuermann et al., 2018).

2.2. Elemental concentrations analysis

Most of the vent fluids and dregs samples reported here have been previously

analyzed for major and trace elements/species (Mg, Ca, Ba, Cl and SO_4) by ion

chromatography (IC) and inductively coupled plasma optical emission spectrometry

(ICP-OES) at the University of Minnesota. All the vent fluid Ba concentrations were

measured by isotope dilution (ID) thermal ionization mass spectrometer (TIMS) and

quadrupole (Quad) ICP-MS at the University of Oxford. The concentration unit of fluid

and dregs [Ba] was normalized to the weight of fluid ([Ba]$_{fluid}$ = fluid Ba μmol/fluid kg;

[Ba]$_{dregs}$ = dregs Ba μmol/fluid kg). For comparison, the data of [Ba] between ID-TIMS

and Quad-ICP-MS show agreement within 1-11% (Fig. S1). Therefore, we mainly use

the ID-TIMS [Ba] data in the discussion unless otherwise specified. Overall, the

173 precision of the elemental concentrations is around 1-3 % RSD. The total Ba

174 concentration was corrected ([Ba]$_{corr}$) by the sum of Ba concentrations in dissolved

175 fluids and dregs:

176 $[Ba]_{corr} = [Ba]_{fluid} + [Ba]_{dregs}$ (1)

177

178 **2.3. Barium isotope analyses**

179 All the fluid solution samples were prepared and analyzed for Ba isotopes and

180 Ba concentrations using ID-TIMS at the University of Oxford. In addition to the fluid

181 samples, two of the dregs samples from MEF and ASHES were also analyzed for Ba

182 isotopes (Table 2). The Ba isotope methods were adapted from previous studies (Hsieh

183 and Henderson, 2017; Bridgestock et al., 2018). In brief, sample solutions, containing

184 ~200 ng of Ba or maximum 200 μL fluid, were weighed, acidified and spiked with

185 ^{137}Ba-^{135}Ba double spike. The samples were dried and re-dissolved in 1mL 3M HCl

186 before purification by cation exchange chromatography (AG50-X8, 200-400 mesh).

187 The overall procedure blank is < 0.1 ng of Ba (n = 3). Barium isotope analyses were

188 performed on a Thermo Finnigan Triton TIMS at the University of Oxford. In this study,

189 Ba isotopic compositions are reported as the δ-notation $\delta^{138/134}$Ba (‰) relative to the

190 National Institute of Standards and Technology (NIST) 3104a standard:

191 $\delta^{138/134}Ba\ (‰) = (^{138}Ba/^{134}Ba_{sample}/^{138}Ba/^{134}Ba_{NIST3104a} - 1) \times 1000$ (2)

192 For comparison, data reported in $\delta^{137/134}$Ba in some previous studies have been

193 converted to $\delta^{138/134}$Ba by multiplying by 1.33.

194 Standards and samples generally show an internal precision between 0.01 and

195 0.02 ‰ (± 2SE, n = 540) during each isotope analysis. The long-term (external)

196 precision and accuracy are monitored with a secondary Ba standard NBS-127 over two

197 years, $\delta^{138/134}$Ba = -0.29 ± 0.02 ‰ (± 2SD, n = 14), which is in agreement with published

198 values in previous studies (Horner et al., 2017; Crockford et al., 2019). We use the

199 repeatability of these standard measurements to assess uncertainty of single

200 measurement, which is generally quoted in this paper as ±0.02‰. Most measurements

201 had similar or better internal uncertainty (0.01-0.02 ‰, ± 2SE) but a small number,

202 with low Ba contents, show larger internal uncertainty, up to 0.08 ‰ (±2 SE). For these

203 samples, we use the internal uncertainty from their measurement.

204

205 **3. Results**

206 The hydrothermal vent fluids display a wide range of Ba concentrations from

207 0.43 to 97.9 μmol/kg and $\delta^{138/134}$Ba values from -0.26 to +0.91 ‰, including both dregs

208 corrected and uncorrected data, in selected hydrothermal fluids from six different vent

209 fields (Table 1; Fig. 3). For comparison, temperature, pH, Mg, Cl, Ca and SO_4 data are

210 provided in Table 1 and Table S1, and seawater data from the North Atlantic (Bates et

211 al., 2017; Hsieh and Henderson, 2017) and North Pacific (Geyman et al. 2019) are also

212 provided. No significant relationship was found between the $\delta^{138/134}$Ba values and

213 temperature, pH, [Mg], [SO_4], [Ca] or [Cl] (all $r^2 < 0.1$). The fluid data show a

214 predictable linear relationship between SO_4 and Mg concentrations, which suggests a

215 conservative mixing between seawater and hydrothermal source fluid lacking these

216 components (Fig. 3a). In contrast, Ba concentrations broadly decrease with increasing

217 SO_4 concentrations due to seawater mixing (Fig. 3b). However, the relationship

218 between Ba and SO_4 concentrations is not linear, which indicates that Ba is removed

219 from solution during the mixing. The fluid $\delta^{138/134}$Ba compositions broadly increase

220 with decreasing Ba concentrations, but this relationship cannot be explained by

221 conservative mixing between seawater and the endmember fluids either (Fig. 3c).

222   Different hydrothermal systems show a wide range of dissolved Ba isotope

223   compositions $\delta^{138/134}$Ba and [Ba] (Table 1; Fig. 3c). Vent fluids from the ultramafic-

224   hosted Rainbow hydrothermal field (36°N, MAR) show $\delta^{138/134}$Ba values from -0.26 to

225   +0.36 ‰, associated with a large gradient of [Ba] changing from 4.54 to 97.9 µmol/kg.

226   In the basalt-hosted EPR, the vent fluids from EPR 9-10°N and EPR 13°N show diverse

227     $\delta^{138/134}$Ba values from +0.02 to +0.40 ‰ with a range of [Ba] from 0.43 to 14.1 µmol/kg.

228   In the JdFR, the $\delta^{138/134}$Ba value is generally much heavier in the MEF and ASHES vent

229   fluids (+0.40 to +0.91 ‰) than is the case for the other vent fluids discussed, while the

230   Ba concentrations (1.65 to 46.1 µmol/kg) are not hugely different from the others.

231   Particulate (dregs) Ba concentrations show a wide range from below < 0.01

232   (below detection limit) to 41.2 µmol/kg. The sum of dregs Ba and dissolved fluid Ba

233   indicates the total content of Ba in the fluids, as calculated by Eq. (1) (Table 1). The

234   fraction of dregs Ba ranges from 2 to 83% of the total Ba. The dregs Ba isotopic

235   compositions $\delta^{138/134}$Ba in two available samples are -0.11 ± 0.02 ‰ and +0.08 ± 0.08

236   ‰, and both values are significantly lighter than their fluid $\delta^{138/134}$Ba values (Table 2).

237   For comparison, the observed $\delta^{138/134}$Ba compositions in hydrothermal barites also

238   show light values (-0.04 and -0.08 ‰, Crockford et al., 2019). The dregs isotope data

239   suggest that precipitation in the samplers has preferentially removed isotopically light

240   Ba from vent fluids, and that needs to be considered for the correction of $\delta^{138/134}$Ba

241   values in the vent fluids (see Discussion 4.2). The dregs corrected and uncorrected [Ba]

242   and $\delta^{138/134}$Ba data are both reported in Table 1 for comparison, but the following

243   discussion is mainly based on the corrected data unless otherwise specified.

244

245   **4. Discussion**

246   **4.1. Barite saturation and precipitation during fluid-seawater mixing**

247   Vent fluid Ba and SO_4 concentrations show that Ba is removed during mixing

248   with seawater (Fig. 3b). Such a correspondence has been observed in previous studies

249   and has been explained by barite ($BaSO_4$) precipitation (Von Damm et al., 1985;

250   Seyfried et al. 2003). Barite is one of the most common minerals formed during the

251   mixing of Ba-bearing hydrothermal vent fluids and SO_4-bearing seawater (Shikazono,

252   1994; Hanor, 2000; Jamieson et al., 2016; Gartman et al., 2019). Barite precipitation

253   also often occurs during the sampling of high-temperature vent fluids as a result of

254   seawater entrainment in the samplers, which has caused difficulty in determining the

255   fluid endmember Ba concentrations (Butterfield and Massoth, 1994; Von Damm et al.,

256   1985; Seyfried et al. 2003; Seyfried et al. 2011). Barite precipitation can also be induced

257   by conductive cooling; reducing temperature decreases barite solubility and hence

258   increases barite precipitation (Blount, 1977; Jamieson et al., 2016; Gartman et al., 2019).

259   Barite solubility experiments and thermodynamic models have been used to

260   study Ba and SO_4 chemistry and assess barite saturation in different marine

261   environments (Church and Wolgemuth, 1972; Blount, 1977; Monnin and Galinier,

262   1988; Monnin, 1999; Monnin et al. 1999; Monnin et al. 2001). In this study, we apply

263   the model of Monnin (1999) to calculate the barite solubility product (K_{sp}), activity

264   coefficient (γ_{BaSO4}) and barite saturation index (Ω_{barite}) in the fluid samples under the

265   condition of mixing with deep seawater (1°C and 500 bar):

266   Ω_{barite} = IAP/K_{sp} (3)

267   where IAP is the ionic activity product:

268   IAP = $[Ba^{2+}]\cdot[SO_4^{2-}]\cdot \gamma^2_{BaSO4}$ (4)

269   where $[Ba^{2+}]$ and $[SO_4^{2-}]$ are the fluid Ba and SO_4 mole concentrations. The model

270   parameters are $LogK_{sp}$ = -9.957 and γ_{BaSO4} = 0.1442 (Monnin, 1999).

271   The modeled curves of Ba and SO_4 concentrations at the equilibrium condition

272    $\Omega_{barite} = 1$ are plotted in Fig. 3b and the calculated Ω_{barite} values are reported in Table

273   S1. Most of the samples after the dregs correction are above the curve and the Ω_{barite}

274   values are greater than or close to 1, which implies that the fluid samples are mostly

275   supersaturated with respect to barite, except for one sample in EPR 9-10°N (Ω_{barite} =

276   0.9). Given that the Ba concentration of this sample is higher than in seawater, where

277   the observed Ω_{barite} value is undersaturated, this suggests low degrees of seawater (and

278   therefore sulfate) entrainment during sampling. As the process of venting evolves,

279   barite precipitation can still occur with increased seawater mixing. The calculated

280   saturation index Ω_{barite} is likely to be overestimated in this study due to the

281   underestimate of solubility, particularly for the high temperature vent fluids.

282   Thermodynamic models show that barite K_{sp} decreases with increasing temperature,

283   but due to ion interactions and speciation changes, the solubility increases with

284   increasing temperature in NaCl bearing fluids (Blount, 1977; Monnin 1999).

285   Nevertheless, the chosen condition (1°C and 500 bar) is likely to represent the end point

286   of barite precipitation in hydrothermal plumes mixing with seawater, which provides

287   constraints on the barite precipitation during the entire process and hence the effective

288   input of hydrothermal Ba to the ocean.

289

290   **4.2. Precipitates in the fluids: correction and assessment of fractionation**

291   Precipitation of "dregs" from hydrothermal vent fluid often occurs in the

292   samplers during cooling and mixing with seawater. Although the mineralogy of dregs

293   is mainly metal sulfides (Metz and Trefry, 2000; Rouxel et al., 2008; Yucel et al., 2011;

294   Gartman et al., 2014; Gartman et al., 2018), Ba sulfide (BaS) is highly soluble in water,

295   which makes BaS unlikely to be the host for Ba in the dregs. One previous study has

296   shown that Ba exists as barite, surrounded by sulfides, in the particles precipitated in

297   vent fluids (Gartman et al., 2018). Ba is also commonly observed as barite in sulfide-

298   rich deposits and chimneys in hydrothermal systems (Koski et al., 1994; Shikazono,

299   1994; Tivey, 2007; James et al., 2014; Jamieson et al., 2016). Although these do not

300   exclude the possibility of having some Ba scavenged onto other mineral surfaces (e.g.

301   MnS) when samples are undersaturated for barite, barite seems to be the most likely

302   mineral to host the majority of Ba in the dregs when samples are supersaturated.

303   Correction for dregs is required to assess the original composition of the fluid

304   prior to precipitation. The calculation also enables an assessment of the isotope

305   fractionation occurring during precipitation. Initial fluid Ba isotope compositions were

306   corrected for precipitation of dregs using the analyses of the two dregs samples (Table

307   2; calculation details in supplementary material S1).

308   The average value of calculated $\Delta^{138/134}Ba_{dregs-fluid}$ is -0.35 ± 0.10 ‰ (2SE, n=2).

309   This agrees with values from barite precipitation in previous experimental studies

310   ($\Delta^{138/134}Ba_{barite-fluid}$ = -0.34 ± 0.09 ‰, von Allmen et al., 2010), consistent with barite

311   being the major phase hosting Ba in the dregs. The results from previous experiments,

312   conducted between 4 and 80°C, have shown that Ba isotope fractionation has no

313   temperature dependence in barite precipitation (Von Allmen et al, 2010; Böttcher et al.,

314   2018). The similarity of observed fractionation at the higher temperatures of dregs

315   precipitation implies that this temperature independence may hold to the in situ

316   temperature of vent fluids (~350°C). Considering the uncertainties, the hydrothermal

317   barite Ba isotope fractionation factor is quite similar to that in pelagic barite

318   ($\Delta^{138/134}Ba_{pelagic-barite-seawater}$ ranging from -0.40 to -0.58 ‰, Hsieh and Henderson, 2017;

319   Horner et al., 2017; Bridgestock et al., 2018). Although the fractionation factor in

320   pelagic barite may be slightly larger, it possibly reflects the different precipitation

13

321   conditions and environment (e.g. microenvironment and bacteria for pelagic barite,

322   Bishop, 1998; Martinez-Ruiz et al., 2018).

323   The corrected $\delta^{138/134}$Ba values in the fluids were made by using the measured

324    $\delta^{138/134}$Ba$_{fluid}$, [Ba]$_{fluid}$ and [Ba]$_{dregs}$ from each sample (Table 1; equation S3), assuming

325   that barite is the major phase hosting Ba in dregs and that it has a constant fractionation

326   factor ($\Delta^{138/134}$Ba$_{hyd\text{-}barite\text{-}fluid}$ = -0.35 ± 0.10 ‰). Ba isotope compositions in four fluid

327   samples are not corrected for dregs due to the lack of dregs [Ba] data. The fractionation

328   factor can also be used in the Ba isotope fractionation model to explain the distribution

329   of hydrothermal vent fluid $\delta^{138/134}$Ba values controlled by barite precipitation during

330   mixing with seawater (Discussion 4.4).

331

332   **4.3. Barium isotopes in endmember vent fluids**

333   Elemental compositions of endmember vent fluids are usually estimated by the

334   intersection of a regression line between elements and Mg or SO$_4$ concentrations at zero.

335   This approach relies on the assumption that endmember vent fluid Mg or SO$_4$ is zero,

336   and that any increase of Mg or SO$_4$ is due to seawater entrainment during sampling or

337   subsurface mixing (e.g. Von Damm et al., 1985). However, it is difficult to use the same

338   approach to determine the Ba compositions of endmember vent fluids due to barite

339   precipitation during mixing with seawater. Even after the dregs correction, the

340   corrected fluid Ba still shows non-conservative behavior (Fig. 3b), which implies that

341   either some barite precipitation has occurred in subsurface prior to venting of the fluids

342   or that there is a low recovery of dregs in the samplers. Thus, we select the vent fluids

343   with the highest Ba concentration (dregs corrected) from each hydrothermal vent field

344   as the estimates of endmember vent fluids, except for EPR9-10ºN which takes the

345   average values of the three highest [Ba] samples. The endmember vent fluid [Ba] and

346     $\delta^{138/134}$Ba values are summarized in Table 3 and Fig. 4.

347   Some difference in the endmember fluid Ba compositions can be found between

348   ultramafic-hosted (Rainbow, MAR 36ºN), basalt-hosted (EPR) and sediment-

349   influenced (MEF) systems. The ultramafic-hosted endmember fluid (Rainbow) has the

350   highest [Ba] and lowest $\delta^{138/134}$Ba values, although peridotite and serpentine, the most

351   common source rocks in the ultramafic-hosted systems, have a much lower Ba

352   concentration ([Ba]: 0.1-1.4 ppm, Andreani et al. 2014) than oceanic basalts ([Ba]: 3.9-

353   160.3 ppm, Gale et al. 2013). However, in a gabbro-bearing ultramafic system, such as

354   Rainbow, the components of plutonic and gabbroic rocks in the subsurface play an

355   important role in buffering the high temperature vent fluid chemistry (Seyfried et al.,

356   2011). These rocks may contain more Ba than the reported values above, but this

357   requires more knowledge of Ba in the ultramafic protolith. No reported $\delta^{138/134}$Ba data

358   are available in peridotite and serpentine for direct comparison. The $\delta^{138/134}$Ba value of

359   the basalt-hosted endmember fluids (EPR) is within the range of mid-ocean ridge basalt

360   (MORB) $\delta^{138/134}$Ba values (+0.02 to +0.15‰) (Nielsen et al., 2018). The MEF vent fluid

361   chemistry has shown the encounter with sediments during the fluid recharge zones,

362   although MEF is not a sedimented MOR system (Lilley et al., 1993; Seyfried et al.,

363   2003). The high $\delta^{138/134}$Ba value seen in the MEF endmember fluid may reflect the

364   influence of sediments.

365   Overall, the endmember fluid $\delta^{138/134}$Ba values, ranging from -0.17 (± 0.07) to

366   +0.09 (± 0.03) ‰, are within the range of $\delta^{138/134}$Ba values in their source rocks

367   (MORBs and altered oceanic crust (AOC): -0.09 to +0.33‰, Nielsen et al., 2018;

368   pelagic sediments: -0.2 to +0.1 ‰, Crockford et al., 2019 and Bridgestock et al., 2018)

369   (Fig. 4b). As expected, water-rock interaction at elevated temperatures and pressures

370   appears to occur without Ba isotope fractionation, and a similar observation has been

371   discovered for Ca isotopes (Scheuermann et al., 2018). Therefore, source rocks may be

372   used to constrain the endmember vent fluid $\delta^{138/134}$Ba values.

373   Although the estimates of endmember vent-fluid Ba concentrations can be

374   affected by the uncertainty of Ba recovery in vent fluids, Ba isotopes may also provide

375   an approach to calculate the hypothetical concentration of the corrected Ba ([Ba]$_{corr}$*)

376   in vent fluids prior to barite precipitation and the recovery of Ba (calculation details in

377   supplementary material S2). The $\delta^{138/134}$Ba-derived hypothetical [Ba]$_{corr}$* and [Mg]

378   values can then be used to extrapolate the endmember fluid [Ba] through a linear

379   regression line at the intercept of zero Mg (Fig. 5). In general, the correlations between

380   the fluid [Ba] and [Mg] are improved when using the [Ba]$_{corr}$* values. The extrapolated

381   endmember fluid [Ba] values also agree with the highest fluid [Ba]$_{corr}$ values observed

382   in each vent field (Table 3), except for MEF (Fig. 5d). In MEF, the [Ba]$_{corr}$* values

383   correlate with the Ca and Cl concentrations in vent fluids (Fig. S3). Vapor rich fluids

384   with dissolved Cl contents below seawater are expected to have low endmember Ba

385   and Ca, because these species tend to partition into the liquid phase in the region of

386   liquid-vapor phase separation (Pester et al., 2015).

387   For future studies, Ba isotopes provide better constraints on the Ba

388   compositions in vent fluids if the endmember fluid $\delta^{138/134}$Ba compositions can be

389   provided. The endmember fluid $\delta^{138/134}$Ba values can be obtained by measuring fluid

390   samples with high Ba recovery and the source rocks for comparison.

391

392   **4.4. Barium isotope fractionation model: effective hydrothermal Ba input**

393   Hydrothermal input of dissolved Ba to the ocean is decreased by removal of Ba

394   due to barite precipitation during mixing between vent fluids and seawater. The impact

of this precipitation on Ba isotopes can be simply modelled using the known

fractionation during barite formation (e.g. von Allmen et al. 2010). This model can be

used to explain the variation of vent fluid $\delta^{138/134}$Ba values, and the expected isotope

composition of Ba after barite precipitation.

We apply a Rayleigh isotope fractionation model:

$$\delta^{138/134}Ba_{fluid} = \Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid} \cdot \ln(f) + \delta^{138/134}Ba_{endmember} \tag{5}$$

where $\delta^{138/134}Ba_{endmember}$ and $\Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid}$ denote the isotope composition of the

endmember fluids and hydrothermal barite isotope fractionation factor ($\Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid}$ = -0.35 ± 0.10 ‰), respectively; f is the fraction of dissolved Ba remaining in

the fluids (f = [Ba]$_{fluid}$/[Ba]$_{endmember}$). The endmember fluid [Ba] and $\delta^{138/134}$Ba values

from Table 3 are taken as the initial composition in each hydrothermal vent field.

A Rayleigh fractionation model is appropriate in this situation, because the

precipitation of barite is rapid and the exchange between formed barite and dissolved

Ba is likely limited. A similar fractionation model has been demonstrated in other

isotopes (e.g. Ca and Zn) in hydrothermal systems (Amini et al., 2008; John et al., 2008;

Syverson et al. 2018).

Vent fluid Ba isotope data mostly fit within the trajectory of the isotope

fractionation model with a constant fractionation factor $\Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid}$ = -0.35 ±

0.10 ‰ (Fig 5). This suggests that the Ba isotope variation in vent fluids is primarily

driven by barite precipitation and that the fractionation factor is relatively constant

between all the vent fields of this study. There are, however, a few samples that cannot

be explained by the fractionation model with the initial $\delta^{138/134}Ba_{endmember}$ compositions.

These samples are mostly diffuse-flow type or have undergone significant phase

separation (Fig. 6). Such samples are likely to have differing initial Ba compositions,

419   and to reflect multiple Ba sources (e.g. non-basaltic Ba) and more complex circulation

420   environments.

421   The model can be used to calculate the Ba isotope compositions of the effective

422   hydrothermal component at the point of mixing where barite precipitation stops (Ω_{barite}

423   < 1) and the remaining hydrothermal dissolved Ba starts to mix conservatively with Ba

424   in seawater. Barite saturation calculations, using a seawater SO_4 concentration of 28

425   mmol/kg, indicate that fluids become undersaturated when [Ba] < 0.2 μmol/kg. We

426   extend the Rayleigh model to this value to assess the Ba isotope compositions at the

427   end point of hydrothermal plumes during mixing with seawater (Fig. 6e-h). These end-

428   point $\delta^{138/134}$Ba compositions, representing the composition of dissolved Ba added to

429   seawater, are high (+1.0 ~ +2.6 ‰), with an average of +1.7 ± 0.7 ‰ (2SD).

430   In addition to barite precipitation, scavenging on to Fe oxyhydroxides and Mn

431   oxides may also remove Ba and cause isotope fractionation in hydrothermal plumes.

432   However, the fraction of Ba associated with the hydrothermal Fe oxyhydroxides is

433   relatively small in hydrothermal plumes (Feely et al. 1996). Barium scavenging onto

434   Fe oxyhydroxides or Mn oxides is likely to be a significantly less prominent process in

435   hydrothermal plumes, than incorporation into barite. Any isotope fractionation

436   associated with this process is unknown and would require future study to provide

437   further constraint.

438   Calculated end-point dissolved Ba compositions ($\delta^{138/134}$Ba = +1.7 ± 0.7 ‰) are

439   notably higher than the range observed in seawater (+0.22 ~ +0.65‰) (Fig. 4b). Such

440   an isotopically heavy Ba could explain the non-conservative mixing seen in Atlantic

441   deep waters (Hsieh and Henderson, 2017).

442

443   **4.5. Hydrothermal Ba isotopes and non-conservative mixing in deep waters**

444   To assess the influence of hydrothermal Ba input on the isotope composition of

445 Atlantic deep-waters, a three endmember mixing model is applied to these waters:

446 $f_{NADW} + f_{AABW} + f_{hyd} = 1$ (6)

447 $[Ba]_{sw} = f_{NADW} [Ba]_{NADW} + f_{AABW} [Ba]_{AABW} + f_{hyd} [Ba]_{hyd}$ (7)

448 $[Ba]_{sw} \cdot \delta^{138/134}Ba_{sw} = f_{NADW} \cdot [Ba]_{NADW} \cdot \delta^{138/134}Ba_{NADW} + f_{AABW} \cdot [Ba]_{AABW} \cdot \delta^{138/134}Ba_{AABW}$

449 $+ f_{hyd} \cdot [Ba]_{hyd} \cdot \delta^{138/134}Ba_{hyd}$ (8)

450 $F_{Ba\_hyd} = f_{hyd} \cdot [Ba]_{hyd} / [Ba]_{sw}$ (9)

451 where the subscripts identify the mixed deep seawater (sw) and each endmember:

452 NADW, AABW and the effective hydrothermal Ba (hyd); f denotes the relative

453 fractions of each endmember water, and F_{Ba_hyd} is the relative fraction of hydrothermal

454 Ba input in the Atlantic deep-waters.

455   The proximity of observed seawater compositions to these three end members

456 constrains the mixture of these components, as illustrated in Fig. 7. The calculated

457 fraction of hydrothermal plume water (f_{hyd}), the effective hydrothermal Ba endmember,

458 is 1.3 ~ 3.6 % in the deep water, taking into account the uncertainty of endmember

459 values. This assumes a combined two-stage water dilution factor of 1.4 ~ 3.6 ($\times 10^4$),

460 firstly from vent fluids to the effective Ba endmember in the hydrothermal plume and

461 then to the deep water, assuming a maximum dilution in the first stage of $\approx$ 500 (i.e.

462 vent fluid [Ba] 100 μmol/kg / 0.2 μmol/kg). The dilution factor is of a similar order of

463 magnitude to the helium-3 dilution, 1.7 ~ 34 ($\times 10^4$): from vent fluids (endmember

464 average ^{3}He: 17.1 pmol/kg, Jean-Baptiste et al., 2004) to deep waters (^{3}He < 0.05 to 1

465 fmol/kg, Ruth et al., 2000 and Lupton, 1998). The calculated fraction of hydrothermal

466 Ba input (F_{Ba_hyd}) consists of 3 ~ 9 % of the Ba in some Atlantic deep-waters. The

467 deviations of seawater Ba isotopes from the conservative deep-water mixing can be

468   explained by different degrees of hydrothermal Ba contributions in deep waters (Fig.

469   7b).

470   The hydrothermal input contributes isotopically heavy Ba to the ocean

471   ($\delta^{138/134}$Ba = +1.7 ± 0.7 ‰) which, if a significant component of the ocean Ba cycle,

472   would be hard to reconcile with a balanced Ba isotope budget. Riverine Ba is the main

473   Ba input to the ocean with a range of measured isotope values from -0.06 to +0.46‰).

474   The major Ba output is biogenetic barite and its burial in marine sediments which has

475   a $\delta^{138/134}$Ba value from -0.21 to +0.11‰. This range overlaps that of rivers (Fig. 4b) but

476   may be somewhat lower on average, so that observed inputs may be isotopically heavier

477   than outputs. The heavy input from hydrothermal Ba implies that either (1)

478   hydrothermal Ba flux is small; or (2) other isotopically heavy sinks are missing. The

479   total global hydrothermal Ba vent flux has been estimated to be 2.40 to 3.35 Gmol/yr

480   (Paytan and Kastner, 1996; Dickens et al., 2003), based on the end-member vent fluid

481   [Ba] prior to barite precipitation (i.e. with Ba concentration > 10 µmol/kg, Von Damm

482   et al., 1985). This flux is about 4 ~ 6 times smaller than the riverine Ba flux (14.75

483   Gmol/yr, Wolgemuth and Broecker, 1970; Dickens et al., 2003). Considering that

484   hydrothermal [Ba], after precipitation of barite, is 0.2 µmol/kg, the effective

485   hydrothermal Ba flux to the global ocean will be much smaller than the initial vent flux.

486   More precise assessments of Ba fluxes and isotopic compositions in other sources (e.g.

487   cold seeps and submarine groundwater discharge) and sinks (e.g. Fe-Mn oxides and

488   oxyhydroxides) are needed to fully constrain the Ba isotope budget in the ocean.

489   Seawater SO_4 plays an important role in barite saturation and hence in

490   determining the influence of hydrothermal Ba input and its non-conservative behavior

491   in the ocean. In an ocean with lower SO_4 concentration than the modern ocean, barite

492   precipitation during mixing would cease at a higher Ba concentration, and consequently

493   lower $\delta^{138/134}$Ba value (Fig. 8). Reconstructions of marine sulfur isotope values suggest

494   that seawater SO_4 concentration may have varied from present levels to much lower

495   concentrations of only a few mmol/kg during the Phanerozoic (Canfield and Farquhar,

496   2009; Turchyn and DePaolo, 2019). These changes could have a large impact on the

497   hydrothermal Ba inputs to the ocean. Deep sea corals (Hemsing et al., 2017; Geyman

498   et al., 2019) and hydrothermal barites (Crockford et al., 2019) can potentially be used

499   to reconstruct water and hydrothermal Ba isotope compositions in the past. The

500   relationship between seawater SO_4 and barite precipitation may allow Ba and Ba

501   isotopes to serve as a tracer to reveal the history of MOR hydrothermal Ba inputs and

502   seawater SO_4 in the ocean.

503

504   **5. Conclusions**

505   We present the first Ba isotope data in MOR hydrothermal vent fluids from

506   numerous hydrothermal systems, including basalt-hosted, ultramafic-hosted and

507   sediment-influenced hydrothermal systems. The vent fluids display a wide range of

508   dissolved Ba concentrations and are generally supersaturated with respect to barite

509   ($\Omega_{barite} > 1$). The endmember initial vent fluid $\delta^{138/134}$Ba values, ranging from -0.17 to

510   +0.09 ‰, agree with the values observed in source rocks, which implies that water-rock

511   interaction has a limited effect on the Ba isotope variation in vent fluids. Barite

512   precipitation removes isotopically light Ba from vent fluids during the mixing between

513   Ba-bearing vent fluids and SO_4-bearing seawater. This mixing follows a Rayleigh

514   fractionation with a fractionation factor of $\Delta^{138/134}$Ba$_{hyd-barite-fluid} = -0.35 \pm 0.10$ ‰. Barite

515   precipitation controls the magnitude and composition of hydrothermal Ba input

516   ultimately added as dissolved Ba to seawater. The effective hydrothermal Ba

517   composition is calculated as [Ba]$_{hyd}$ = 0.2 μmol/kg and $\delta^{138/134}$Ba$_{hyd}$ = +1.7 ± 0.7 ‰.

518 Such an isotopically heavy Ba can explain the non-conservative mixing seen in deep

519 waters, with hydrothermal input around 3 ~ 9 % of the Ba in some Atlantic deep waters.

520 The relationship between vent fluid Ba and seawater SO_4 makes Ba isotopes a potential

521 tracer to reconstruct the history of MOR hydrothermal Ba inputs and seawater SO_4

522 concentrations in the past.

523

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874 **Table and figure captions**

875 **Table 1** Vent fluid and particle (dregs) sample information, temperature, Mg, SO$_4$ and

876 Ba concentrations and Ba isotope compositions.

877 **Table 2** Vent fluid and particle (dregs) Ba concentration, isotope composition and

878 fractionation factor.

879 **Table 3** Summary of calculated Ba compositions in endmember fluids.

881 **Figure 1.** Compilations of seawater [Ba] and $\delta^{138/134}$Ba data below 2000 m in the

882 Atlantic and Southern Oceans. Deep-water $\delta^{138/134}$Ba and [Ba] data in the South

883 Atlantic (2000~3000 m) show deviations (~ 0.1 ‰ $\delta^{138/134}$Ba offsets), highlighted by

884 the yellow arrow and circle, from the conservative mixing line (the dashed line and

885 grey band ±2σ) between NADW and AABW during the N-S Atlantic water transport.

886   Additional Ba inputs (e.g. hydrothermal input) may be responsible for the apparent non-

887   conservative behavior. The Ba compositions of NADW ([Ba] $\approx$ 51 nmol/kg; $\delta^{138/134}$Ba

888    $\approx$ +0.45‰) and AABW ([Ba] $\approx$ 103 nmol/kg; $\delta^{138/134}$Ba $\approx$ +0.25‰) have been assessed

889   by Hsieh and Henderson (2017) and Bates et al. (2017). Compiled data are from Horner

890   et al. (2015), Bates et al. (2017), Hsieh and Henderson (2017), Bridgestock et al. (2018)

891   and Hemsing et al., (2018).

892

893   **Figure 2.** Location of MOR hydrothermal vent fields and sampling years in this study.

894

895   **Figure 3.** Ba, Mg and SO$_4$ concentrations and Ba isotope compositions for MOR

896   hydrothermal vent fluids from MAR (Rainbow 36°N and TAG 26°N), EPR (9-10°N

897   and 13°N) and JdFR (MEF and ASHES) vent systems. **(a)** Hydrothermal vent fluid

898   [SO$_4$] versus [Mg] (dashed line represents conservative mixing between vent fluids and

899   seawater). **(b)** Plot of vent fluid [Ba] versus [SO$_4$], and the expected curve for barite

900   saturation (Ω_{barite} = 1) at deep-water T-P condition (1°C and 500 bar), demonstrating

901   that many samples are super-saturated for barite. The circles show the focused-flow

902   fluids and the triangles show the diffuse-flow samples. The closed symbols show the

903   dregs corrected fluid Ba compositions (equation 1) and the open symbols show all the

904   non-corrected data. Seawater and vent fluid conservative mixing is illustrated in dashed

905   lines. Removal of Ba by barite precipitation during mixing with seawater is highlighted

906   by the purple arrow. **(c)** Plot of Ba isotopes and Ba/Mg ratios for vent fluids (both dregs

907   corrected and non-corrected; Section 4.2) indicating Ba isotope fractionation during

908   mixing of vent fluids and seawater and resulting barite precipitation. The data show the

909   largest range of $\delta^{138/134}$Ba (-0.26 ~ +0.91 ‰) so far seen in any marine environment.

910   Seawater Ba concentration and isotope data are the average values (between 2000 and

30

911   3000m) from the North Atlantic (BATS, Hsieh and Henderson, 2017) and North Pacific

912   (SAFe, Geyman et al., 2019).

913

914   **Figure 4. (a)** Comparisons of vent fluid $\delta^{138/134}$Ba values between different vent fields.

915   The open red diamonds are the measured values and the solid red diamonds are the

916   dregs corrected values. The black squares are the estimates of endmember vent fluid in

917   each field. **(b)** Comparisons of $\delta^{138/134}$Ba values in marine systems: seawater (Horner

918   et al., 2015; Hsieh and Henderson, 2017; Bates et al., 2017; Horner et al., 2017;

919   Bridgestock et al., 2018; Hemsing et al., 2018; Geyman et al., 2019; Cao et al., 2020),

920   rivers (Cao et al., 2016; Hsieh and Henderson, 2017; Gou et al., 2020), MORBs and

921   AOC (Nielsen et al., 2018; Nielsen et al., 2020), pelagic sediments (Bridgestock et al.,

922   2018; Crockford et al., 2019; Nielsen et al., 2020), and hydrothermal vent fluids (this

923   study). The hydrothermal vent fluid data show the largest range of $\delta^{138/134}$Ba (-0.26 ~

924   +0.91 ‰) so far seen in marine environments. The effective hydrothermal input

925    $\delta^{138/134}$Ba (+1.7 ± 0.7‰, red square) is extrapolated by barite saturation and Ba isotope

926   fractionation models (Discussion 4.4).

927

928   **Figure 5.** Barium versus magnesium in the (a) Rainbow, (b) MEF, (c) EPR 9-10°N,

929   and (d) EPR 13°N hydrothermal vent fluids. The blue open circles show the dregs

930   corrected Ba concentrations ([Ba]$_{corr}$) and the red closed circles show the $\delta^{138/134}$Ba-

931   derived hypothetical Ba concentration ([Ba]$_{corr}$*) prior to barite precipitation. The

932   dashed lines show the linear regressions through the [Ba] and [Mg] data, which are used

933   to extrapolate the endmember fluid [Ba] at the intercept of zero Mg (±1SD).

934

935 **Figure 6.** Ba isotopes and concentrations in the Rainbow, EPR 9-10°N, EPR 13°N and

936 MEF hydrothermal vent fluids with seawater mixing, Rayleigh fractionation and barite

937 saturation models. **(a-d)** The data of Ba isotopes and 1/[Ba] show increased $\delta^{138/134}$Ba

938 as [Ba] in vent fluids decreases. A Rayleigh fractionation model with a fractionation

939 factor $\Delta^{138/134}Ba_{hyd-barite-fluid}$ = -0.35 ± 0.10 ‰ (orange and blue lines) is applied to fit the

940 data. The initial endmember fluid compositions are taken from Table 3. The closed and

941 open circles are the dregs corrected and uncorrected fluid Ba compositions respectively.

942 Samples outside the range of the model trajectory are labeled individually. They are

943 likely to be affected by phase separation (PS), evidenced by low [Cl] and [Ca] (Table

944 S1), or diffuse-flow (DF) in a more complex circulation environment. Foustoukos et al.

945 (2009) have also noticed that Smoke & Mirrors (S&M) may have a different circulation

946 environment from other focused-flow vents in the MEF vent field. **(e-h)** Extrapolation

947 of curves in (a-d) to the [Ba] values at the end point of hydrothermal plumes during

948 mixing with seawater. Barite saturation values (Ω_{barite} = 1) are shown by green vertical

949 lines. Once [Ba] becomes under-saturated (< 0.2 μmol/kg, Ω_{barite} < 1), remaining Ba in

950 the plumes starts to mix conservatively with seawater, as indicated by the black arrow.

951 The effective hydrothermal Ba isotope compositions are labeled in green. Seawater Ba

952 data are from Hsieh and Henderson (2017) and Geyman et al. (2019). NA and NP stand

953 for the North Atlantic and the North Pacific seawaters respectively. The brown bends

954 refer to the range of $\delta^{138/134}$Ba values in MORBs (+0.02 to +0.15‰; Nielsen et al., 2018).

955

956 **Figure 7.** Estimated hydrothermal Ba input in the deep Atlantic Ocean. **(a)** Three

957 endmembers mixing model. The red square shows the hydrothermal value with its

958 uncertainty ([Ba] ≈ 200 nmol/kg; $\delta^{138/134}$Ba = +1.7 ± 0.7‰), and the blue and green

959 squares show the compositions of NADW ([Ba] ≈ 51 nmol/kg; $\delta^{138/134}$Ba ≈ +0.45‰)

960   and AABW ($[Ba] \approx 103$ nmol/kg; $\delta^{138/134}Ba \approx +0.25‰$) respectively (Hsieh and

961   Henderson, 2017; Bates et al., 2017). The yellow square shows the mixed seawater

962   composition (SW_{SA}) between 2000 and 3000 m depth from the South Atlantic ($[Ba] \approx$

963   78 nmol/kg; $\delta^{138/134}Ba \approx +0.39‰$) (Horner et al., 2015; Hsieh and Henderson, 2017).

964   Dashed mixing lines between the hydrothermal Ba and deep water endmembers are

965   labeled with open circles to indicate the fractions of hydrothermal Ba input (F_{Ba_hyd}) in

966   the deep water Ba (0-100%). The non-hydrothermal Ba fractions between NADW and

967   AABW are labeled with crosses. As the uncertainty of the hydrothermal $\delta^{138/134}Ba$

968   composition is large, models are calculated against the average value (orange dashed

969   lines) as well as the high and low ends of the values (grey dashed lines). **(b)** The impact

970   of hydrothermal Ba input on the distribution of deep-water $[Ba]$ and $\delta^{138/134}Ba$ (Fig. 1).

971   The dashed lines show the fraction of hydrothermal Ba input (F_{Ba_hyd}) in the deep water

972   Ba (0-10%). The fraction values on display are calculated against the average

973   hydrothermal $\delta^{138/134}Ba$ (+1.7‰). The original data of the yellow square shown in (a)

974   is highlighted in the yellow area.

975

976   **Figure 8.** Relationship between seawater SO_4 concentrations and the input

977   compositions of effective hydrothermal Ba ($[Ba]_{hyd}$ and $\delta^{138/134}Ba_{hyd}$) in the ocean. The

978   yellow curve shows $[Ba]_{hyd}$, based on the barite saturation model ($\Omega_{barite} = 1$) at deep-

979   water T-P condition (1°C and 500bar) (Monnin, 1999). The blue curve shows

980     $\delta^{138/134}Ba_{hyd}$ with uncertainties (the grey curves), based on a fractionation factor

981   ($\Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid} = -0.35 \pm 0.10$ ‰) and $[Ba]_{hyd}$ in the Ba isotope fractionation

982   model. For illustrative purposes, the initial composition for the fractionation is taken

983   from the average values of endmember fluids (Table 3) as a generic composition ($[Ba]$

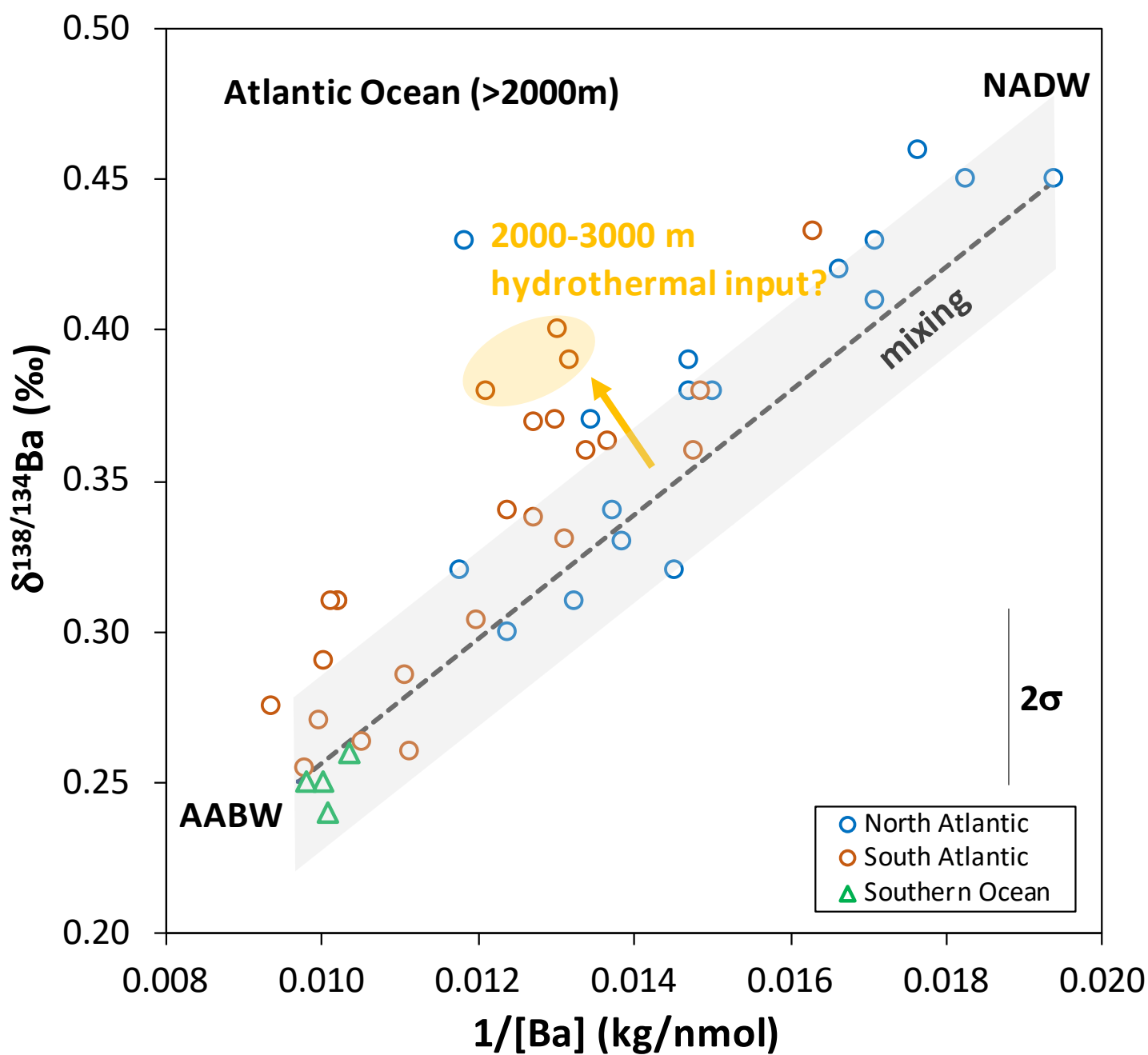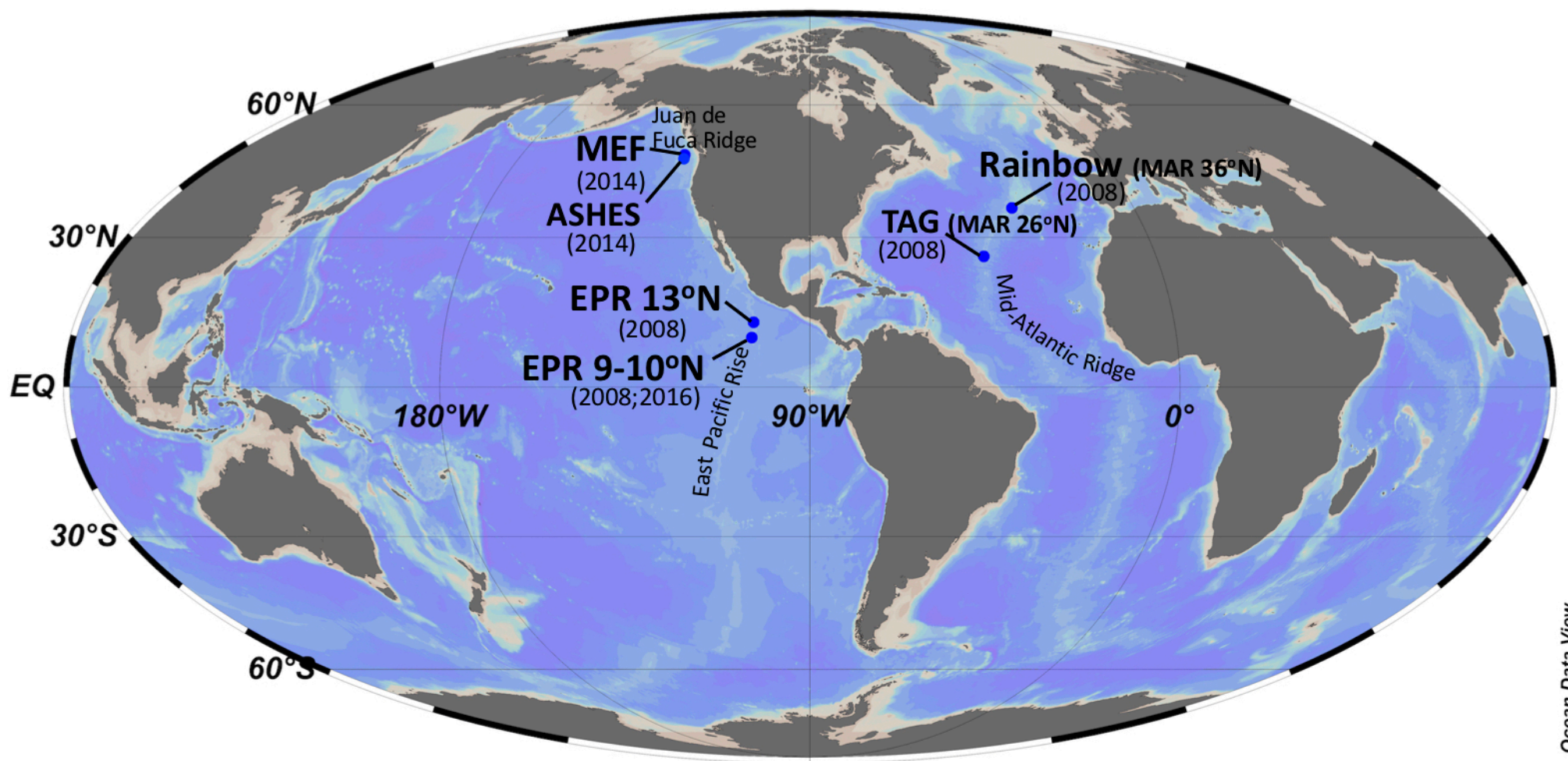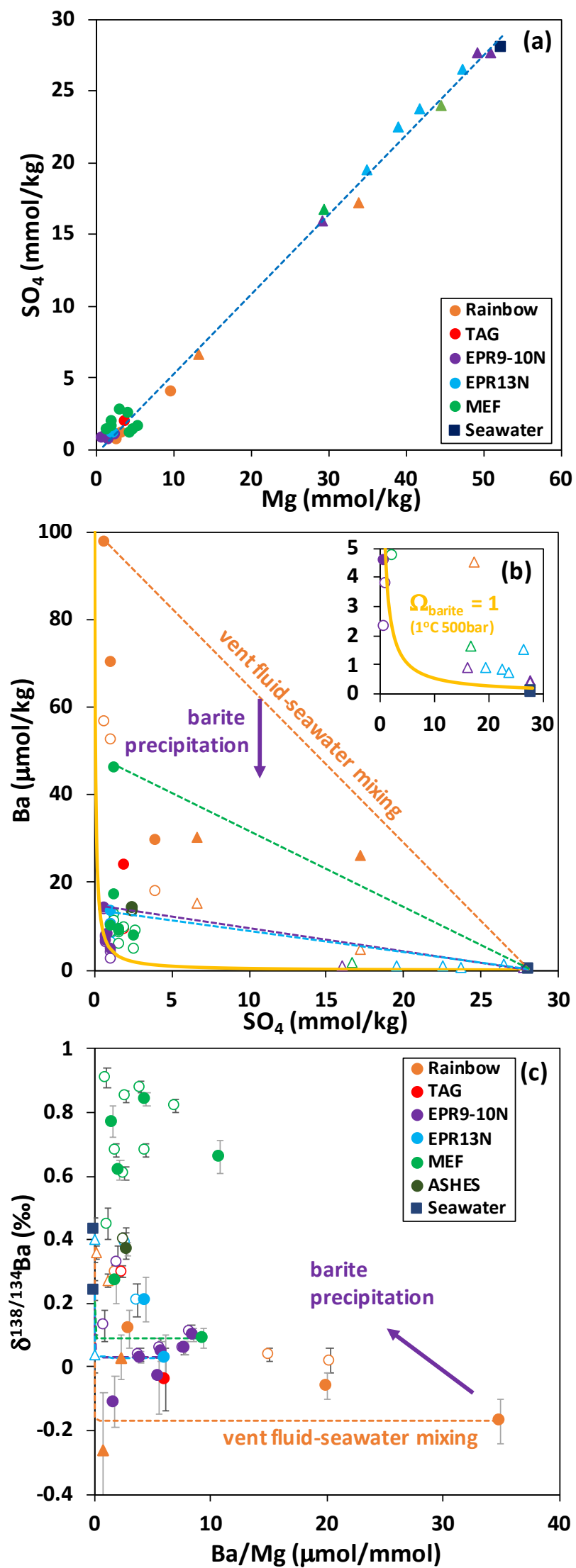984 $= 42$ μmol/kg and $\delta^{138/134}Ba = -0.07$ ‰).

Figure 1

Figure 2

Figure 3

Figure 4

(a)

ASHES

MEF

EPR13N

EPR9-10N

TAG

Rainbow

$\delta^{138/134}$Ba (‰)

(b)

Seawater

Rivers

MORBs

AOC

Pelagic sediments

Hydrothermal vent fluids

effective input
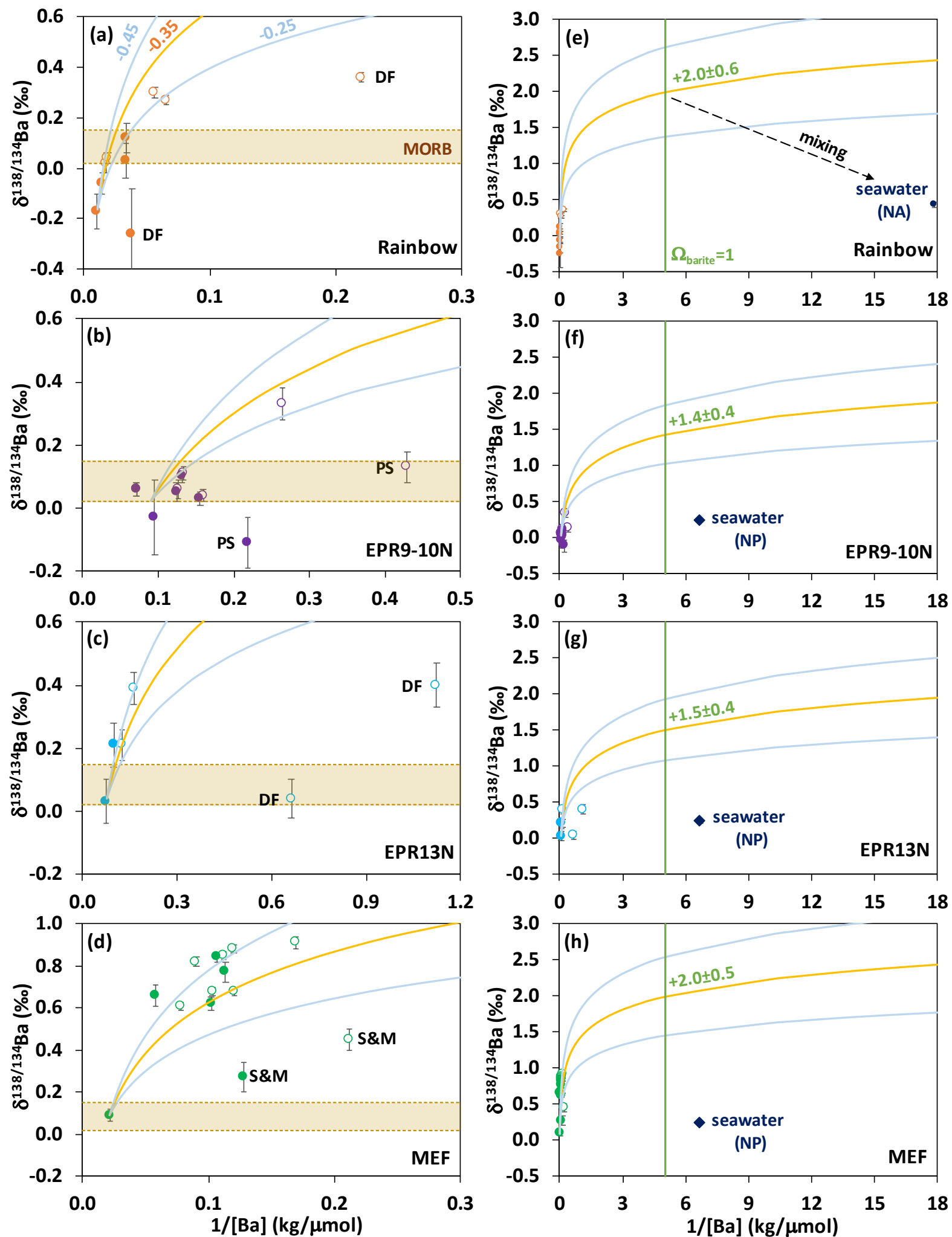to the ocean

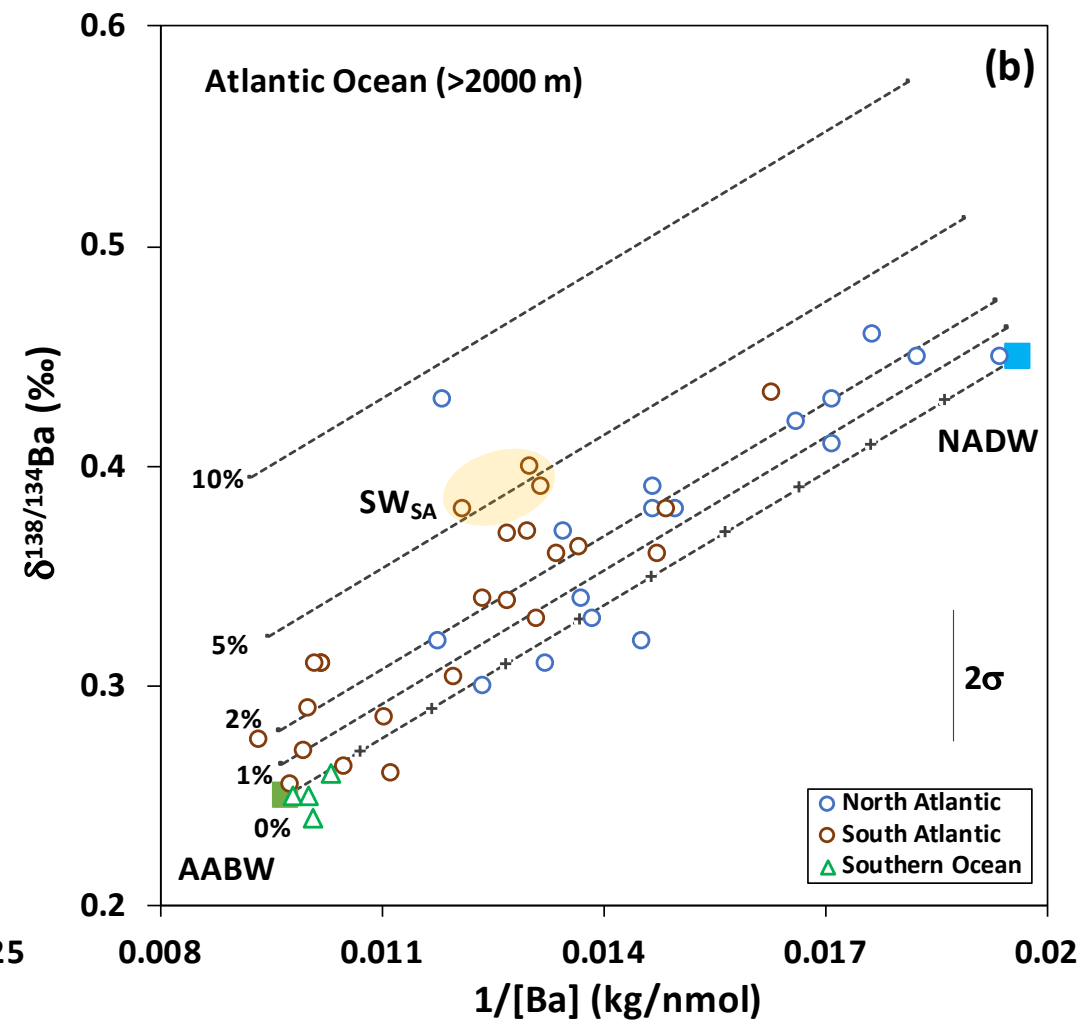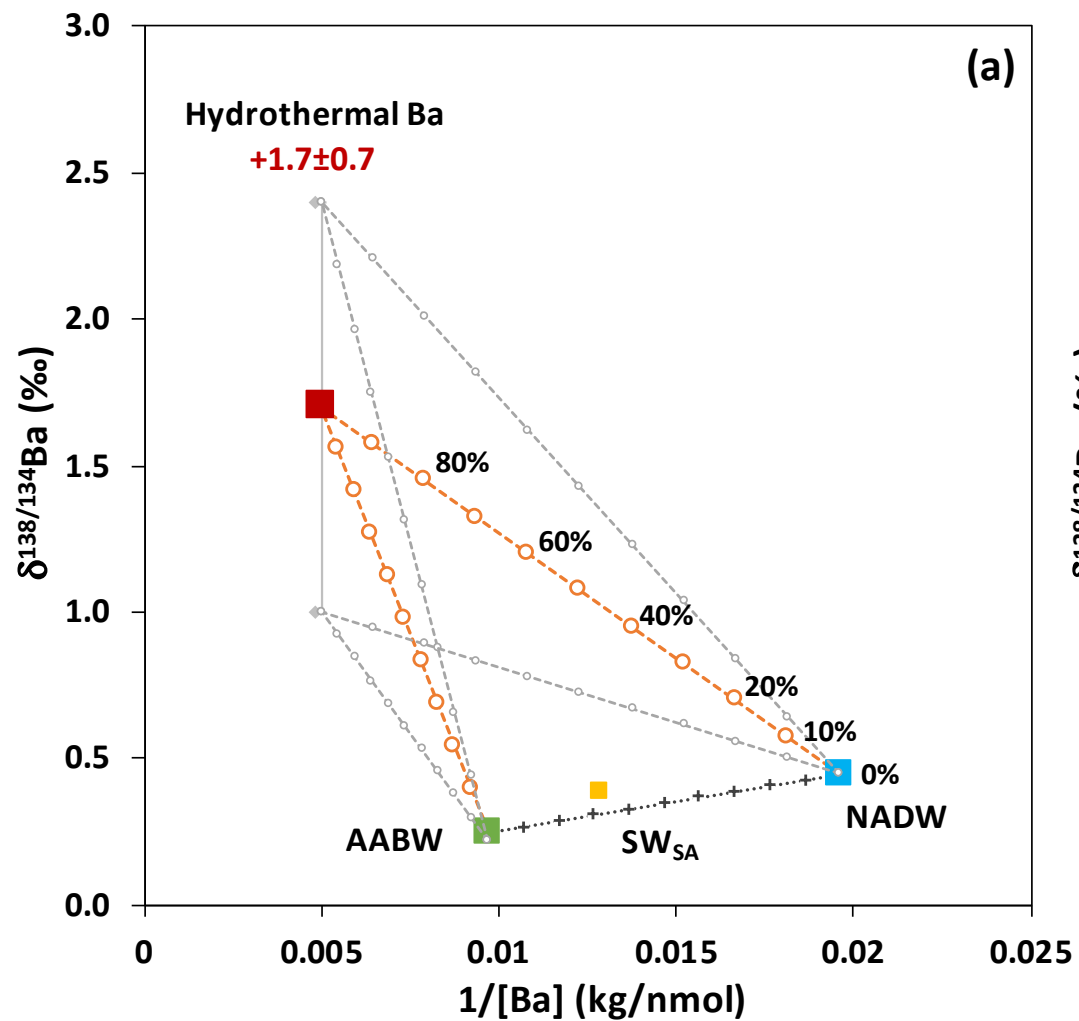$\delta^{138/134}$Ba (‰)

Figure 5
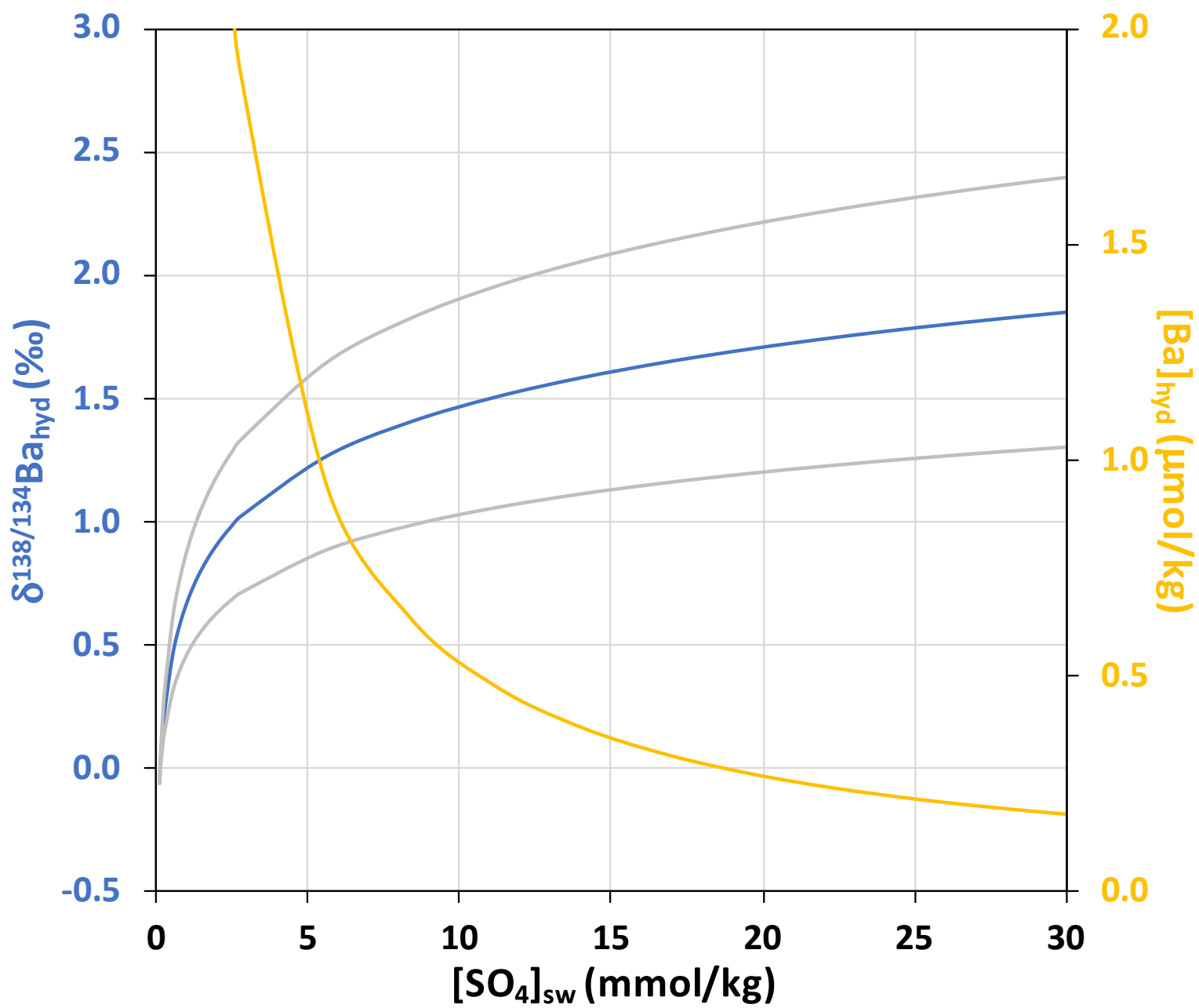
Figure 6

Figure 7

Figure 8

Table 1 Vent fluid and particle (dregs) sample information, temperature, Mg, SO_4 and Ba concentrations and Ba isotope composition.

Vent	Type[a]	Sample ID dive-sampler	Temp (oC)	Mg (mmol/kg)	SO_4 (mmol/kg)	Ba-uncorr (µmol/kg)	$\delta^{138/134}$Ba uncorr	±2S.D.[J]	Ba-dregs[c] (µmol/kg)	Ba-corr[e] (µmol/kg)	$\delta^{138/134}$Ba corr[e]	±2S.D.
Rainbow (MAR 36°N) (2008) (36.23°N, 33.90°W)[f]												
Guillaume, X4	FF	352-IGT4	354	2.8	0.66	56.7	0.02	0.04	41.2	97.9	-0.17	0.07
Regner	FF	353-IGT2	323	9.8	4.02	17.8	0.30	0.02	11.8	29.6	0.12	0.06
CMSP&P	FF	354-IGT3	365	3.5	1.15	52.6	0.04	0.02	17.6	70.2	-0.06	0.04
Ecurie	DF	354-IGT4	66	33.8	17.2	4.54	0.36	0.02	21.7	26.2	-0.26	0.18
Ecurie	DF	354-IGT8	128	13.2	6.61	15.3	0.27	0.02	15.0	30.3	0.03	0.07
TAG (MAR 26°N) (2008) (26.14°N, 44.83°W)												
TAG	FF	363-IGT5	366	3.9	2.0	9.22	0.30	0.02	14.8	24.0	-0.04	0.10
EPR9-10°N (2008) (9.83°N, 104.29°W)[g]												
Bio-9	FF	4386-IGT6	330	1.9	1.1	3.78	0.33	0.05	6.68	10.5	-0.03	0.12
Tica	DF	4388-IGT5	25	29.3	16.0	0.89[b]						
Ty-Io	FF	4393-IGT6	304	2.6	1.07	2.33	0.13	0.05	2.26	4.59	-0.11	0.08
Crab-Spa	DF	4394-IGT6	23	49.3	27.7	0.46[b]						
Ty-Io	DF	4397-IGT5	13	51	27.7	0.43[b]						
EPR9-10°N (2016) (9.83°N, 104.29°W)												
Bio-9	FF	4837-IGTD	374	1.8	0.7	13.9	0.06	0.02	0.17[d]	14.1	0.06	0.02
Bio-9	FF	4838-IGTB	373	1.6	0.8	6.27	0.04	0.02	0.17[d]	6.44	0.03	0.02
Pvent	FF	4838-2-6	363	0.9	0.8	7.47	0.11	0.02	0.17[d]	7.64	0.10	0.02
Pvent	FF	4841-2-4	354	1.4	0.9	7.92	0.06	0.03	0.16[d]	8.08	0.05	0.03
EPR13°N (2008) (12.83°N, 103.95°W)[g,h]												
Grand Bonum	FF	4389-IGT5	350	2.2	1.1	8.02	0.21	0.05	5.35	13.4	0.03	0.07
Dorian	DF	4391-MG		39.1	22.5	0.88[b]						
Dorian	FF	4392-IGT5	344	2.3	1.1	6.17	0.39	0.05	4.02	10.2	0.21	0.07
Jumeaux	DF	4392-MG	148	34.9	19.5	0.89	0.40	0.07				
Ph05	DF	4392-IGT6	148	41.8	23.7	0.72[b]						
Actinoir	DF	4391-MW	74	47.3	26.5	1.51	0.04	0.06				
MEF (2014) (47.95°N, 129.10°W)[g,i]												
Bastille	FF	4743-C	321	5.6	1.63	5.92	0.91	0.03	2.90	8.82	0.77	0.05
Bastille	FF	4743-2	317	4.9	1.34	12.8	0.61	0.02	33.3	46.1	0.09	0.03
Lobo	FF	4743-D	333	1.6	1.36	11.1	0.82	0.02	6.20	17.3	0.66	0.05
TP	FF	4743-E	334	2.1	1.59	8.36	0.88	0.02	1.00	9.36	0.84	0.02
Lobo	FF	4744-1	335	3.3	2.7	8.93	0.85	0.02				
Dante	FF	4744-2	329	2.2	1.91	9.72	0.68	0.02				
Sully Flange	DF	4743-4	267	29.4	16.7	1.65[b]						
Puffer	FF	4743-5	280	4.5	1.14	8.32	0.68	0.02	1.50	9.82	0.62	0.03
S and M	FF	4743-6	291	4.2	2.57	4.73	0.45	0.05	3.10	7.83	0.27	0.07
ASHES (2014) (45.93°N, 130.01°W)[g,i]												
Inferno	FF	4741-D	299	5	2.47	13.2	0.40	0.02	1.10	14.3	0.37	0.02
Seawater												
N Atlantic BATS (2000-3000m, n=3) (Hsieh and Henderson, 2017)							0.06	0.43	0.04			
N Pacific SAFe (2000-3000m, n=5) (Geyman et al., 2019)							0.15	0.24	0.03			

[a]Vent type FF: focused-flow; DF: diffuse-flow. [b][Ba] fluid data analyzed by Quad-ICP-MS. [c]Dregs [Ba] is normalized to the volume of samplers. [d]Dregs [Ba] data analyzed by ID-TIMS. [e]Ba data are corrected for dregs Ba removal and isotope fractionation (Discussion 4.2). [f,g,h,i]More sample information and other data are available in [f]Seyfried et al. (2011), [g]Scheuermann et al., (2018), [h]Pester et al. (2011) and [i]Syverson et al. (2017). [J]The external reproducibility is 0.02 (±2SD).

Table 2 Vent fluid and particle (dregs) Ba concentration, isotope composition and fractionation factor.

| Sample | | Fluids-uncorr | | Dregs | | Fluids-corr | | dregs-fluid |
Vent	ID	Ba (μmol/kg)	$\delta^{138/134}$Ba ±2S.D.	Ba (μmol/kg)	$\delta^{138/134}$Ba ±2S.D.	Ba (μmol/kg)	$\delta^{138/134}$Ba ±2S.D.	$\Delta^{138/134}$Ba ±2S.D.
MEF (2014)								
Bastille	4743-2	12.8	0.61 ± 0.02	33.3	-0.11 ± 0.02	46.1	0.09 ± 0.03	-0.40 ± 0.03
ASHES (2014)								
Inferno	4741-D	13.2	0.40 ± 0.02	1.1	0.08 ± 0.08	14.3	0.37 ± 0.02	-0.30 ± 0.08
Mean (±2SE)								**-0.35 ± 0.10**

Table 3 Summary of calculated Ba compositions in endmember fluids.

Hydrothermal systems	Endmember fluids		
	Ba (μmol/kg)	Ba* (μmol/kg)	$\delta^{138/134}$Ba
MAR Rainbow (36°N)	98	92 ± 7	-0.17
EPR 9-10°N[a]	11	10 ± 2	0.03
EPR 13°N	13	16 ± 2	0.03
JdFR MEF	46	70 ± 6	0.09

[a]Values based on the mean of three highest [Ba] samples
*Estimates based on the extrapolations at zero Mg (Fig. 5)

Barium isotopes in mid-ocean ridge hydrothermal vent fluids: a source of isotopically heavy Ba to the ocean

Supplementary material

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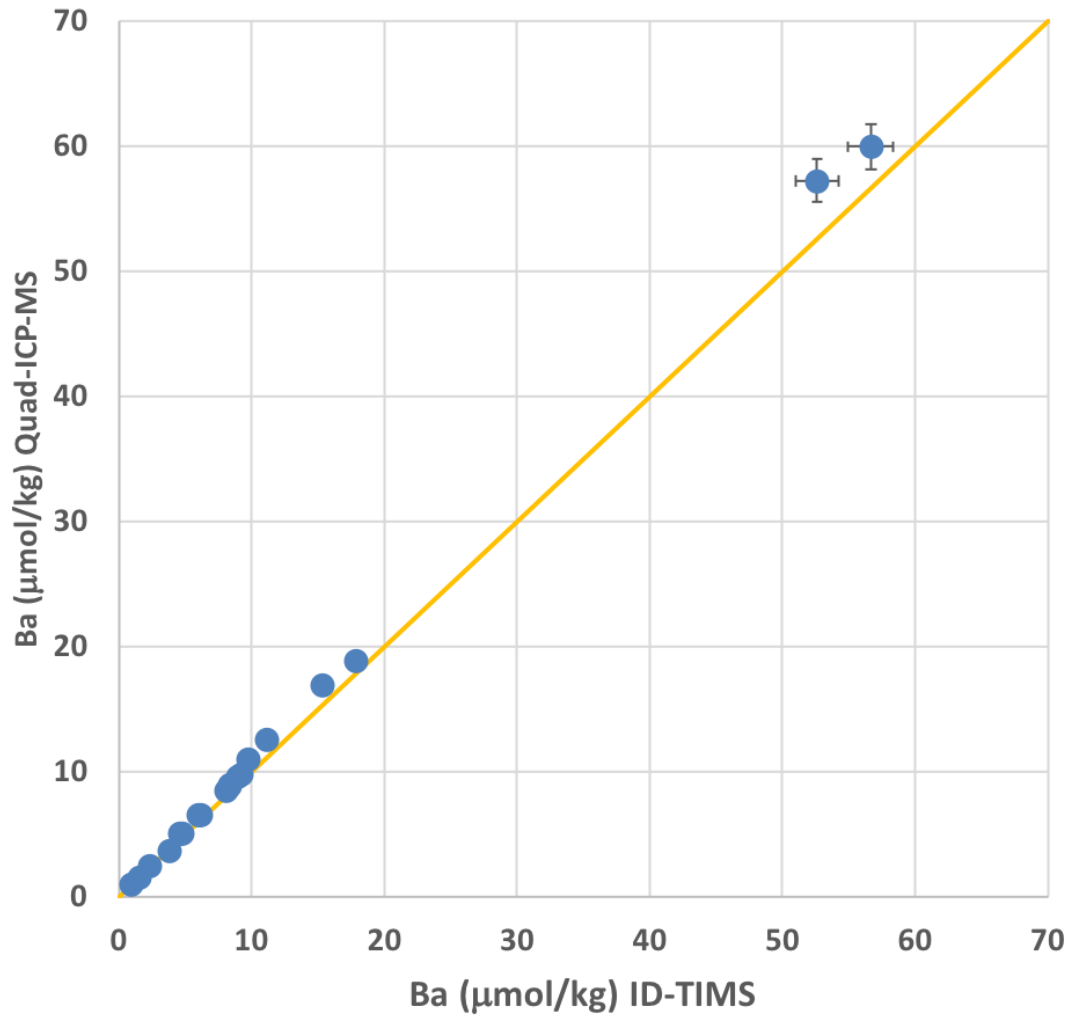***Corresponding author: yu-te.hsieh@earth.ox.ac.uk**

Figure S1. Comparisons of hydrothermal vent fluid Ba concentration data by Quad-ICP-MS and ID-TIMS. The data are generally agreed between the two methods within 1-11%. The offset may reflect the sample dilution and matrix effects between the Quad-ICP-MS and ID-TIMS analyses. The orange line is 1:1, and the error bars are ±3% (1SD).

S1. Calculating dregs corrected vent fluid $\delta^{138/134}$Ba and $\Delta^{138/134}$Ba values

To calculate the dregs corrected vent fluid Ba isotopic compositions, two dregs samples from MEF (4743-2) and ASHES (4741-D) were analyzed for Ba isotopes to reconstruct the corrected fluid $\delta^{138/134}$Ba and to calculate the isotope effect $\Delta^{138/134}$Ba$_{\text{dregs-fluid}}$ on the samples. The dregs corrected fluid Ba isotopic composition ($\delta^{138/134}$Ba$_{\text{corr}}$) is calculated as:

$$\delta^{138/134}\text{Ba}_{\text{corr}} = f \cdot \delta^{138/134}\text{Ba}_{\text{fluid}} + (1\text{-}f) \cdot \delta^{138/134}\text{Ba}_{\text{dregs}} \tag{S1}$$

$$f = [\text{Ba}]_{\text{fluid}}/[\text{Ba}]_{\text{corr}} \tag{S2}$$

where f is the fraction of dissolved Ba in the total fluid Ba and (1-f) is the fraction of dregs Ba. The instantaneous isotope fractionation factor between fluid and dregs is calculated using the Rayleigh isotope fractionation model:

$$\Delta^{138/134}\text{Ba}_{\text{dregs-fluid}} = (\delta^{138/134}\text{Ba}_{\text{fluid}} - \delta^{138/134}\text{Ba}_{\text{corr}}) / \ln(f) \tag{S3}$$

The dregs corrected fluid [Ba] ranges from 6.44 to 97.9 μmol/kg when the dregs fraction is recovered (Table 1), and the fraction of dissolved Ba (f) varies between 0.17 and 0.98 in the vent fluids. For two samples MEF and ASHES, their $\delta^{138/134}$Ba$_{\text{dregs}}$ and $\delta^{138/134}$Ba$_{\text{fluid}}$ compositions and the dissolved Ba fraction f were used to calculate the isotope fractionation factor $\Delta^{138/134}$Ba$_{\text{dregs-fluid}}$ between dregs and fluids. The calculated $\Delta^{138/134}$Ba$_{\text{dregs-fluid}}$ values are -0.40 ± 0.02 ‰ (4743-2) and -0.30 ± 0.08 ‰ (4741-D), with an average value of -0.35 ± 0.10 ‰ (2SE, n=2), considering the uncertainty of [Ba] and $\delta^{138/134}$Ba values (Table 2).

As vent fluids generally have a much higher Ba concentration ([Ba] > 10 μmol/kg) than seawater, the Ba contribution from the seawater component in this calculation is mostly negligible. For example, using Mg as a conservative tracer to estimate the component of seawater in vent fluids and assuming that seawater [Ba] = 0.1 μmol/kg, the estimate of seawater contribution is < 0.1% of total Ba in all of the focused-flow samples of this study.

For the diffuse-flow samples, due to a high degree of seawater entrainment, seawater Ba contribution varies from 0.1 to 25%, which may affect the corrections of vent fluid Ba isotope composition. In this study, the majority of diffuse-flow data is reported as uncorrected only due to the absence of dregs. For future studies of Ba in diffuse-flow vent fluids, the seawater component should be considered.

S2. Using $\delta^{138/134}$Ba values to calculate the corrected Ba concentrations ([Ba]$_{corr}$*) prior to barite precipitation in vent fluids

Even after the dregs correction (see above), the corrected fluid Ba concentrations still show non-conservative behavior (Fig. 3b), which implies that either some barite precipitation has occurred in the subsurface prior to venting of the fluids or there is a low recovery of dregs in the samplers. Although it is not possible to separate the Ba loss between these two processes, when the endmember vent fluid $\delta^{138/134}$Ba values can be obtained, Ba isotopes may provide a new approach to calculate the total loss of Ba and the hypothetical concentration of the corrected Ba ([Ba]$_{corr}$*) in vent fluids prior to barite precipitation using a Rayleigh isotope fractionation model:

$$[Ba]_{corr}* = [Ba]_{fluid} / exp[(\delta^{138/134}Ba_{fluid} - \delta^{138/134}Ba_{corr}*) / \Delta^{138/134}Ba_{hyd\text{-}barite\text{-}fluid}] \qquad (S4)$$

where [Ba]$_{fluid}$ and $\delta^{138/134}$Ba$_{fluid}$ are the measured Ba concentrations and Ba isotope compositions in vent fluids (before dregs correction); $\Delta^{138/134}$Ba$_{hyd\text{-}barite\text{-}fluid}$ is the hydrothermal barite isotope fractionation factor ($\Delta^{138/134}$Ba$_{hyd\text{-}barite\text{-}fluid}$ = -0.35 ± 0.10 ‰); and $\delta^{138/134}$Ba$_{corr}$* is the corrected Ba isotope composition prior to barite precipitation in vent fluids. Without barite precipitation, the $\delta^{138/134}$Ba$_{corr}$* values should be a result of simple mixing between the endmember vent fluids and seawater (Fig. 3c). As mentioned in supplementary material S1, the endmember fluid Ba concentrations are generally several orders of magnitude higher than seawater, Ba contribution from seawater is < 0.1% of total

Ba in most of the mixed vent fluids in this study. Therefore, the $\delta^{138/134}Ba_{corr}*$ values can be assumed to be the same as the endmember fluid $\delta^{138/134}Ba$ values in each vent field. In this study, the agreement between the endmember fluid and source rock $\delta^{138/134}Ba$ values implies that these estimates of the endmember fluid $\delta^{138/134}Ba$ values in Table 3 are not unreasonable. The recovery of Ba after the dregs correction can also be estimated by comparing the dregs corrected $[Ba]_{corr}$ (equation 1) and the $\delta^{138/134}Ba$-derived $[Ba]_{corr}*$ values.

The estimates of $[Ba]_{corr}*$ values and the recovery of Ba after the dregs correction are reported in Table S1 and Fig. S2 for comparison. The recovery of Ba varies from 12 to 130% after the dregs correction, with an average of 71%. It is noted that the vent fluids from MEF and Rainbow seem to have slightly poor Ba recovery (Fig. S2). This calculation has only been applied to the fluid samples that are available with Ba isotope data and the endmember $\delta^{138/134}Ba$ values in Rainbow, EPR and MEF vent fields, except for two samples (Ty-lo 4939-IGT6 and S&M 4743-6) as the endmember $\delta^{138/134}Ba$ values are not applicable (discussed in Section 4.4 and Fig. 5).

Figure S2. Comparisons of the corrected Ba concentrations in vent fluids between the dregs correction ($[Ba]_{corr}$) and the $\delta^{138/134}Ba$-derived hypothetical Ba concentration ($[Ba]_{corr}*$) before barite precipitation. The 1:1 dashed line refers to 100% recovery. Data below the line indicate a low Ba recovery, which could be due to the loss of Ba as barite precipitation in the subsurface prior to venting or in the samplers.
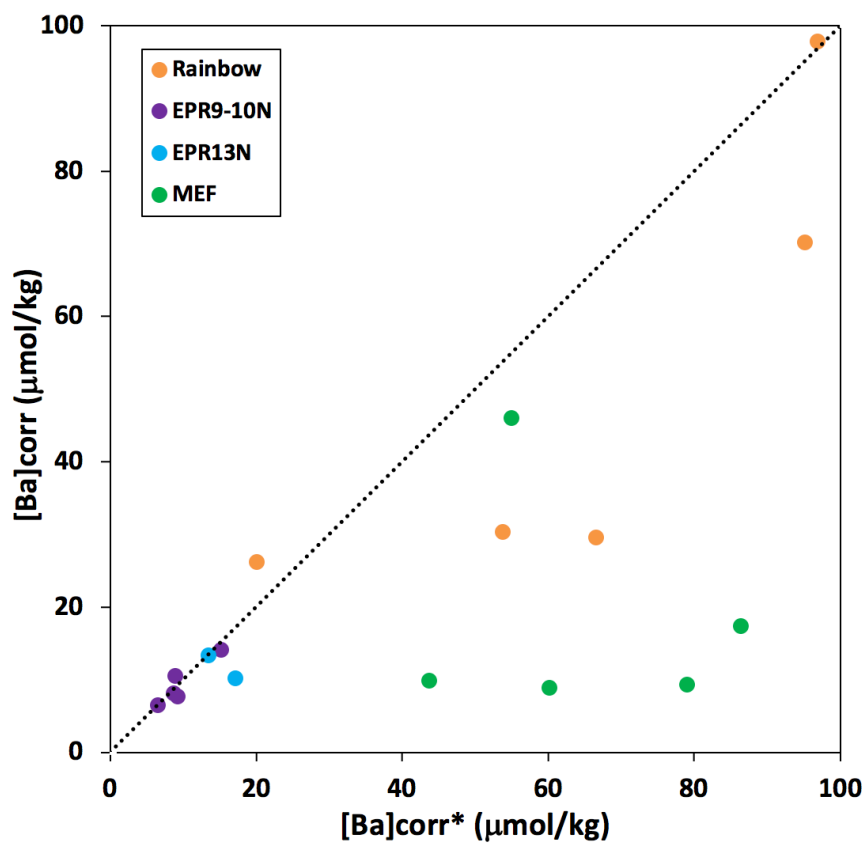
Figure S3. Comparisons of the corrected Ba concentrations between the dregs correction ($[Ba]_{corr}$) and the $\delta^{138/134}$Ba-derived hypothetical Ba concentration ($[Ba]_{corr}*$) prior to barite precipitation in the MEF vent fluids. The estimates of $[Ba]_{corr}*$ values show a better correlation with (a) [Ca] and (b) [Cl] than the dregs corrected [Ba], which may be a result of phase separation partitioning these species between the vapor and liquid phases.

Table S1 Vent fluids pH, Mg, Cl, Ca, SO$_4$, Ba and barite saturation index.

Vent	Type	Sample ID	pH (25°C)	Mg mmol/kg	Cl mmol/kg	Ca mmol/kg	SO$_4$ mmol/kg	Ba µmol/kg uncorr	Ba corr	Ba corr*	Ba Recovery (%) corr/corr*	Ω_{barite} T=1°C; P=500bar[a] uncorr	Ω_{barite} corr
Rainbow (MAR 36°N) (2008) (36.23°N, 33.90°W)													
Guillaume, X4	FF	352-IGT4	3.31	2.8	756	67.9	0.66	56.7	97.9	96.9	101	7.0	12.2
Regner	FF	353-IGT2	3.54	9.8	733	59.7	4.02	17.8	29.6	66.6	44	13.5	22.4
CMSP&P	FF	354-IGT3	3.36	3.5	751	66.8	1.15	52.6	70.2	95.2	74	11.4	15.2
Ecurie	DF	354-IGT4	5.05	33.8	631	34.1	17.2	4.54	26.2	20.0	131	14.7	85.1
Ecurie	DF	354-IGT8	3.23	13.2	717	55.5	6.61	15.3	30.3	53.8	56	19.1	37.8
TAG (MAR 26°N) (2008) (26.14°N, 44.83°W)													
TAG	FF	363-IGT5	3.63	3.9	632	39.4	2.0	9.22	24.0			3.5	9.1
EPR9-10°N (2008) (9.83°N, 104.29°W)													
Bio-9	FF	4386-IGT6	3.23	1.9	313	13.9	1.1	3.78	10.5	8.9	118	0.8	2.2
Tica	DF	4388-IGT5		29.3	366	9.94	16.0	0.89				2.7	
Ty-Io	FF	4393-IGT6	3.91	2.6	165	5.92	1.07	2.33	4.59			0.5	0.9
Crab-Spa	DF	4394-IGT6	5.72	49.3	521	10.1	27.7	0.46				2.4	
Ty-Io	DF	4397-IGT5	6.52	51	533	10.0	27.7	0.43				2.2	
EPR9-10°N (2016) (9.83°N, 104.29°W)													
Bio-9	FF	4837-IGTD	3.35	1.8	285	9.58	0.7	13.9	14.1	15.2	93	1.8	1.9
Bio-9	FF	4838-IGTB	3.13	1.6	268	9.97	0.8	6.27	6.44	6.5	99	0.9	1.0
Pvent	FF	4838-2-6	3.67	0.9	313	11.0	0.8	7.47	7.64	9.3	82	1.1	1.2
Pvent	FF	4841-2-4	3.47	1.4	324	11.2	0.9	7.92	8.08	8.7	93	1.3	1.4
EPR13°N (2008) (12.83°N, 103.95°W)													
Grand Bonum	FF	4389-IGT5	3.34	2.2	642	44.2	1.1	8.02	13.4	13.4	100	1.7	2.8
Dorian	DF	4391-MG		39.1	519	12.9	22.5	0.88				3.7	
Dorian	FF	4392-IGT5	3.49	2.3	466	21.2	1.1	6.17	10.2	17.1	59	1.3	2.1
Jumeaux	DF	4392-MG		34.9	473	11.4	19.5	0.89		2.5		3.3	
Ph05	DF	4392-IGT6	5.78	41.8	552	11.8	23.7	0.72				3.2	
Actinoir	DF	4391-MW		47.3	528	10.7	26.5	1.51		1.5		7.5	
MEF (2014) (47.95°N, 129.10°W)													
Bastille	FF	4743-C	3.73	5.6	447	24.6	1.63	5.92	8.82	60.2	15	1.8	2.7
Bastille	FF	4743-2	3.74	4.9	435	24.5	1.34	12.8	46.1	55.0	84	3.2	11.6
Lobo	FF	4743-D	4.34	1.6	527	40.0	1.36	11.1	17.3	86.4	20	2.9	4.4
TP	FF	4743-E	4.33	2.1	510	38.4	1.59	8.36	9.36	79.0	12	2.5	2.8
Lobo	FF	4744-1	4.38	3.3	532	39.1	2.7	8.93		77.4		4.5	
Dante	FF	4744-2	4.43	2.2	513	37.8	1.91	9.72		51.9		3.5	
Sully Flange	DF	4743-4	5.62	29.4	497	15.8	16.7	1.65				5.2	
Puffer	FF	4743-5	3.72	4.5	437	23.4	1.14	8.32	9.82	43.7	22	1.8	2.1
S and M	FF	4743-6	4.27	4.2	484	30.0	2.57	4.73	7.83			2.3	3.8
ASHES (2014) (45.93°N, 130.01°W)													
Inferno	FF	4741-D	3.79	5	689	45.5	2.47	13.2	14.3			6.1	6.6

[a]Barite saturation model conditions and parameters: T=1°C; P=500 bar; LogK = -9.957; γ = 0.1442 (Monnin 1999).

*The $\delta^{138/134}$Ba-derived hypothetical Ba concentrations in vent fluids prior to barite precipitation.