

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

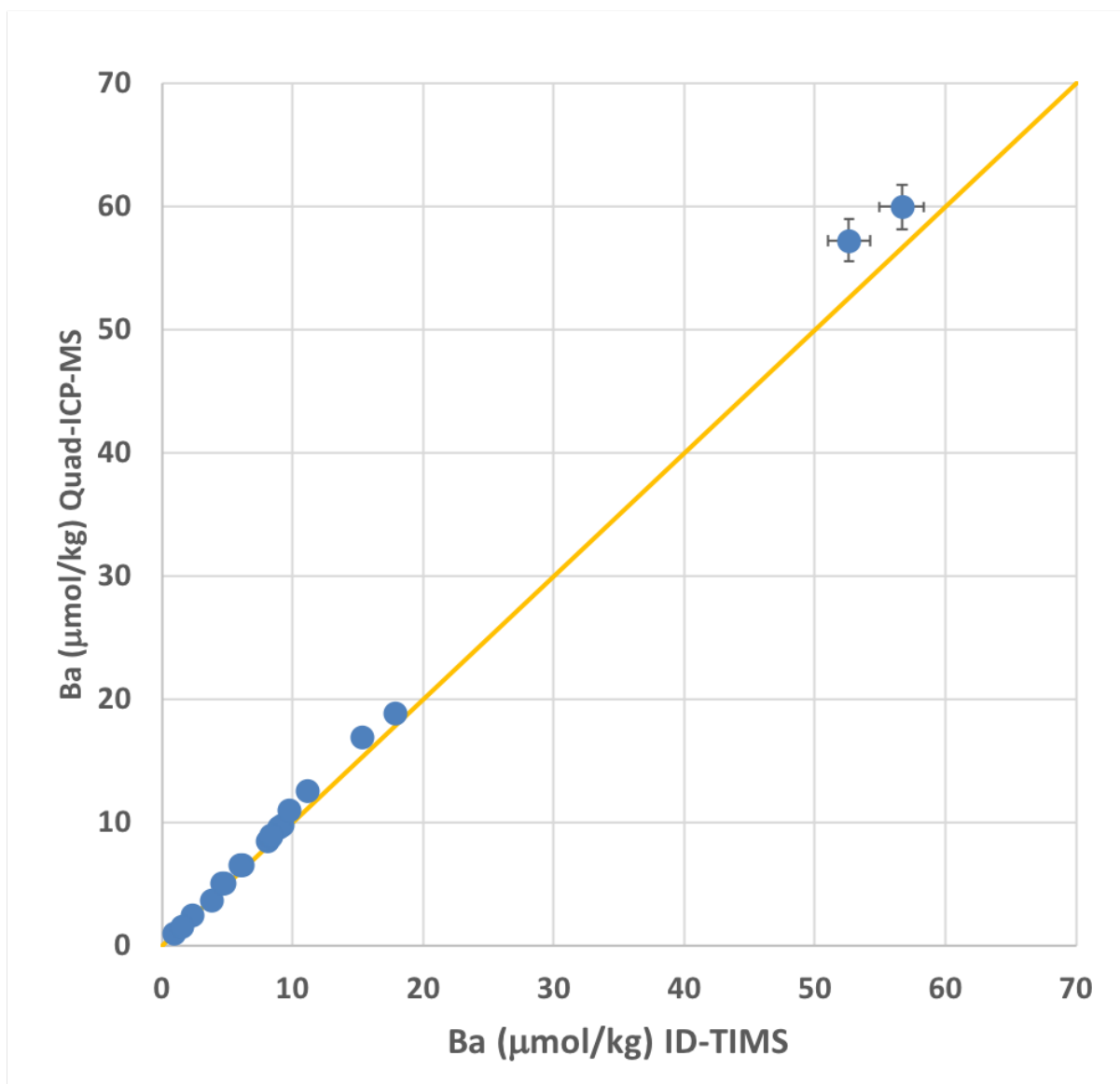
**Supplementary material**

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**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  $\pm 3\%$  (1SD).

## S1. Calculating dregs corrected vent fluid $\delta^{138/134}\text{Ba}$ and $\Delta^{138/134}\text{Ba}$ 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  $\delta^{138/134}\text{Ba}$  and to calculate the isotope effect  $\Delta^{138/134}\text{Ba}_{\text{dregs-fluid}}$  on the samples. The dregs corrected fluid Ba isotopic composition ( $\delta^{138/134}\text{Ba}_{\text{corr}}$ ) is calculated as:

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

$$f = [\text{Ba}]_{\text{fluid}} / [\text{Ba}]_{\text{corr}} \quad (\text{S2})$$

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:

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

The dregs corrected fluid  $[\text{Ba}]$  ranges from 6.44 to 97.9  $\mu\text{mol/kg}$  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  $\delta^{138/134}\text{Ba}_{\text{dregs}}$  and  $\delta^{138/134}\text{Ba}_{\text{fluid}}$  compositions and the dissolved Ba fraction  $f$  were used to calculate the isotope fractionation factor  $\Delta^{138/134}\text{Ba}_{\text{dregs-fluid}}$  between dregs and fluids. The calculated  $\Delta^{138/134}\text{Ba}_{\text{dregs-fluid}}$  values are  $-0.40 \pm 0.02 \text{ ‰}$  (4743-2) and  $-0.30 \pm 0.08 \text{ ‰}$  (4741-D), with an average value of  $-0.35 \pm 0.10 \text{ ‰}$  (2SE,  $n=2$ ), considering the uncertainty of  $[\text{Ba}]$  and  $\delta^{138/134}\text{Ba}$  values (Table 2).

As vent fluids generally have a much higher Ba concentration ( $[\text{Ba}] > 10 \mu\text{mol/kg}$ ) 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  $[\text{Ba}] = 0.1 \mu\text{mol/kg}$ , 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 $\delta^{138/134}\text{Ba}$ values to calculate the corrected Ba concentrations ( $[\text{Ba}]_{\text{corr}^*}$ ) prior to barite precipitation in vent fluids**

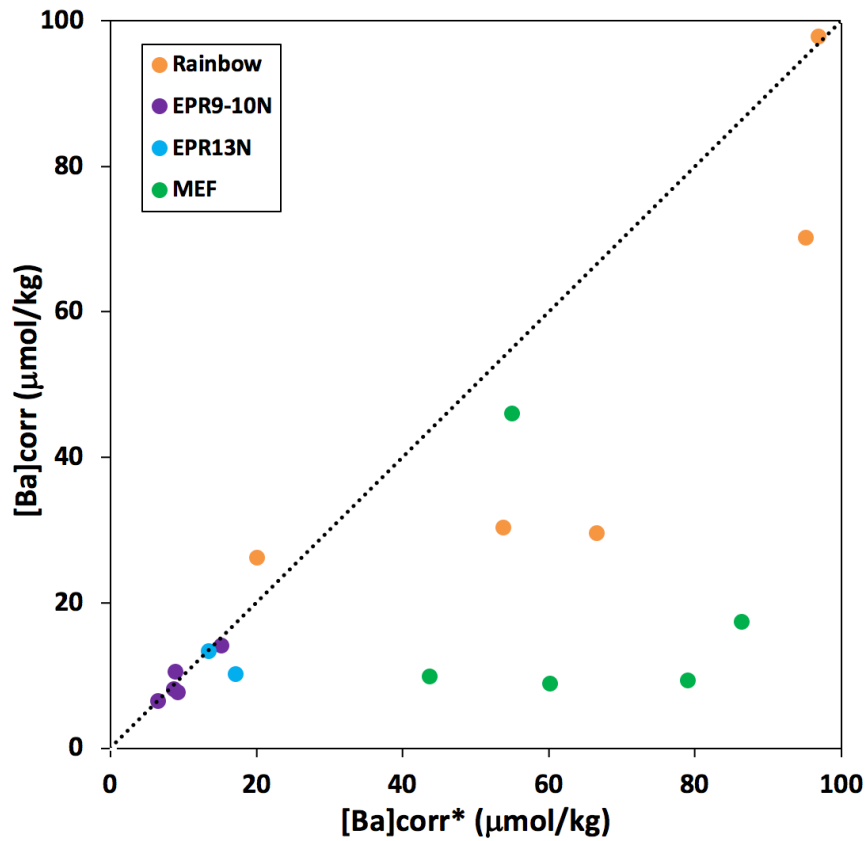
Even after the dregs correction (see above), the corrected fluid Ba concentrations still show non-conservative behavior (Fig. 3b), which implies that either some barite precipitation has occurred in the subsurface prior to venting of the fluids or there is a low recovery of dregs in the samplers. Although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

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

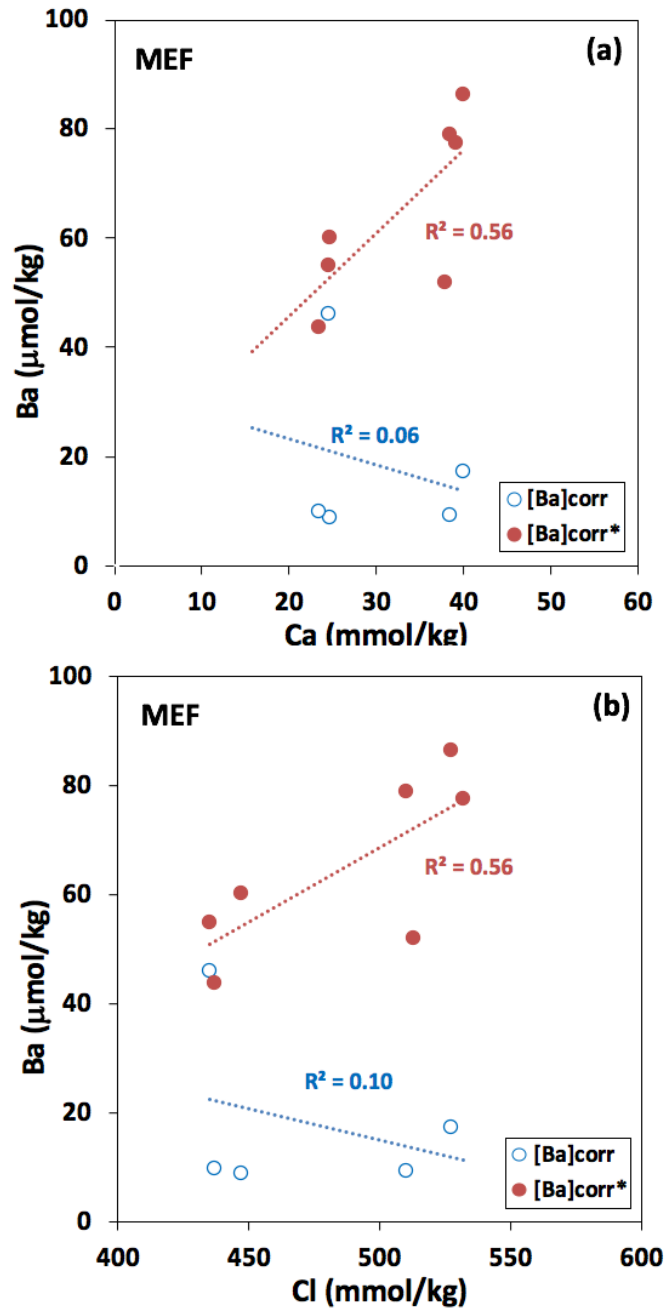
where  $[\text{Ba}]_{\text{fluid}}$  and  $\delta^{138/134}\text{Ba}_{\text{fluid}}$  are the measured Ba concentrations and Ba isotope compositions in vent fluids (before dregs correction);  $\Delta^{138/134}\text{Ba}_{\text{hyd-barite-fluid}}$  is the hydrothermal barite isotope fractionation factor ( $\Delta^{138/134}\text{Ba}_{\text{hyd-barite-fluid}} = -0.35 \pm 0.10 \text{ ‰}$ ); and  $\delta^{138/134}\text{Ba}_{\text{corr}^*}$  is the corrected Ba isotope composition prior to barite precipitation in vent fluids. Without barite precipitation, the  $\delta^{138/134}\text{Ba}_{\text{corr}^*}$  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  $\delta^{138/134}\text{Ba}_{\text{corr}}^*$  values can be assumed to be the same as the endmember fluid  $\delta^{138/134}\text{Ba}$  values in each vent field. In this study, the agreement between the endmember fluid and source rock  $\delta^{138/134}\text{Ba}$  values implies that these estimates of the endmember fluid  $\delta^{138/134}\text{Ba}$  values in Table 3 are not unreasonable. The recovery of Ba after the dregs correction can also be estimated by comparing the dregs corrected  $[\text{Ba}]_{\text{corr}}$  (equation 1) and the  $\delta^{138/134}\text{Ba}$ -derived  $[\text{Ba}]_{\text{corr}}^*$  values.

The estimates of  $[\text{Ba}]_{\text{corr}}^*$  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  $\delta^{138/134}\text{Ba}$  values in Rainbow, EPR and MEF vent fields, except for two samples (Ty-lo 4939-IGT6 and S&M 4743-6) as the endmember  $\delta^{138/134}\text{Ba}$  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  $\delta^{138/134}\text{Ba}$ -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 ( $[\text{Ba}]_{\text{corr}}$ ) and the  $\delta^{138/134}\text{Ba}$ -derived hypothetical Ba concentration ( $[\text{Ba}]_{\text{corr}}^*$ ) prior to barite precipitation in the MEF vent fluids. The estimates of  $[\text{Ba}]_{\text{corr}}^*$  values show a better correlation with (a)  $[\text{Ca}]$  and (b)  $[\text{Cl}]$  than the dregs corrected  $[\text{Ba}]$ , which may be a result of phase separation partitioning these species between the vapor and liquid phases.