- Precipitation and growth of barite within hydrothermal vents from the
 Endeavour Segment, Juan de Fuca Ridge
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17 Abstract

- 18 Hydrothermal vents form on the seafloor as a result of cooling and mixing of hot, mineral-rich
- 19 hydrothermal fluids with cold seawater. Amongst the major sulfide and sulfate minerals that
- 20 precipitate at the vent site, barite (BaSO₄) is unique because it requires the direct mixing of Ba-
- 21 rich hydrothermal fluid with sulfate rich seawater in order for precipitation to occur. Because
- 22 of its extremely low solubility, barite crystals preserve geochemical fingerprints associated with
- 23 conditions of formation. Here, we present data from petrographic and geochemical analyses of
- 24 hydrothermal barite from the Endeavour Segment of the Juan de Fuca Ridge, northeast Pacific
- 25 Ocean, in order to determine the physical and chemical conditions under which barite
- 26 precipitates within seafloor hydrothermal vents. Petrographic analyses of 22 barite-rich
- 27 samples show a range of barite crystal morphologies: dendritic and acicular barite forms near
- 28 the exterior vent walls, whereas larger bladed and tabular crystals occur within the interior of
- 29 chimneys. A two component mixing model based on Sr concentrations and ⁸⁷Sr/⁸⁶Sr of both

30 seawater and hydrothermal fluid, combined with ⁸⁷Sr/⁸⁶Sr data from whole rock and laser-31 ablation ICP-MS analyses of barite crystals indicate that barite precipitates from a mixture 32 containing as low as 17% and as high as 88% hydrothermal fluid component, relative to 33 seawater. Geochemical modelling of the relationship between aqueous species concentrations and degree of fluid mixing indicates that Ba²⁺ availability is the dominant control on crystal 34 35 growth. Dendritic barite forms from fluids with a saturation index greater than ~0.6, which 36 corresponds to fluids with less than a 40% hydrothermal component, whereas more euhedral 37 crystals will form from at lower levels of supersaturation associated with greater contributions 38 of hydrothermal fluid. Fluid inclusions within barite indicate formation temperatures of 39 between ~120 and 240°C during barite crystallization. The comparison of fluid inclusion 40 formation temperatures to modelled mixing temperatures indicates that conductive cooling of 41 the vent fluid accounts for 60 – 120°C reduction in fluid temperature. Strontium zonation 42 within individual barite crystals records fluctuations in the amount of conductive cooling within 43 chimney walls that may result from cyclical oscillations in hydrothermal fluid flux.

44

45 Introduction

Heat from shallow magmatic activity drives the circulation of seawater through oceanic crust
along volcanically-active mid-ocean ridges, arcs, and back-arc basins (Baker et al., 1995;
Hannington et al., 2005). As fluids circulate, they are heated, and react chemically with the
surrounding rock, resulting in leaching and transport of dissolved chemical constituents from
the underlying substrate to the seafloor. Hydrothermal chimneys and mounds form on the

seafloor at sites where the high temperature, focused hydrothermal fluid discharges. Here,
mineral precipitation is driven by the mixing of the hot vent fluid with local cold seawater
(Hannington et al., 1995; Von Damm, 1990).

54 The composition of the substrate is a major control on both vent fluid composition and the mineralogy of the hydrothermal deposits that form on the seafloor. The primary minerals that 55 56 typically make up vent structures are sulfides such as pyrite, sphalerite, chalcopyrite, 57 pyrrhotite, sulfates such as barite and anhydrite, and amorphous silica. These minerals 58 precipitate either from dissolved constituents within the hydrothermal fluids (e.g., pyrite precipitated from dissolved Fe²⁺ and S²⁻), from dissolved constituents within locally heated 59 seawater (e.g., anhydrite precipitated from dissolve Ca²⁺ and SO₄²⁻), or from dissolved 60 constituents within both fluids (e.g., barite precipitated from Ba²⁺ in hydrothermal fluid that has 61 62 mixed with SO₄²⁻-rich seawater) (Hannington et al., 2005; Tivey et al., 1999; Von Damm, 1990). 63 Mineral precipitation is driven mainly by the changes in temperature, pH, fO_2 , and 64 concentration of dissolved ions that accompany the mixing of hot hydrothermal fluid and cold seawater, although fluid temperature can also be affected by conductive cooling and heating 65 66 (Hannington et al., 1995; Ruiz-Agudo et al., 2015; Tivey, 1995; Tivey and McDuff, 1990; Tivey et 67 al., 1999). The occurrence of specific minerals or mineral assemblages within a chimney thus 68 largely reflects the physicochemical properties of the local fluid at the time of precipitation. 69 High-temperature minerals (minerals that precipitate at temperatures above ~300°C, such as 70 chalcopyrite, pyrrhotite, wurtzite) precipitate primarily along inner fluid conduits, where there 71 is limited infiltration of cold seawater (Hannington et al., 1995). The porous outer chimney 72 walls typically contain a lower-temperature (<~300°C) suite of minerals (e.g., sphalerite, barite,

and amorphous silica) that precipitate as a result of a higher degree of mixing with seawater,
and/or conductive cooling of the hydrothermal fluid (Hannington et al., 1995; Tivey et al.,
1999).

76 Barite and other low-temperature minerals dominate the early and late growth stages of a hydrothermal chimney, which are characterized by lower hydrothermal fluxes and fluid 77 78 temperatures (Hannington et al., 1995; Tivey et al., 1990). However, precipitation of these low-79 temperature minerals will still occur during high-temperature venting, often in the exterior 80 walls of a chimney where extensive mixing with seawater occurs (Hannington et al., 1991; 81 Hannington and Scott, 1988). For barite, precipitation occurs when the product of the 82 concentrations of Ba²⁺ (from the hydrothermal fluid) and SO₄²⁻ (from seawater) exceed the 83 solubility constant of the mixed fluid (Blount, 1977). End-member concentrations of Ba in 84 hydrothermal fluids from Main Endeavour Field have been measured at concentrations of up to 85 30 µmol/kg (Seyfried et al., 2003), indicating significant enrichment of Ba relative to ambient 86 seawater (0.1 µmol/kg) resulting from leaching of Ba during hydrothermal alteration of basalt 87 (Chan et al., 1976; Kim and McMurtry, 1991). Modern seawater contains ~28 mmol/kg of 88 dissolved sulfate, whereas sulfate concentrations in endmember hydrothermal fluids are 89 generally near zero as a result of precipitation of anhydrite within the crust and the thermo-90 chemical reduction of remaining sulfate during high-temperature reactions with basalt (Halevy 91 et al., 2012; Seyfried et al., 2003). Because barite is the only major mineral phase in hydrothermal chimneys whose components are sourced from both hydrothermal fluid and 92 93 seawater, the occurrence, and crystallographic and geochemical properties of barite can

94 provide insights into fluid mixing and the physicochemical conditions that drive mineral95 precipitation within the walls of actively-forming chimneys.

96 Strontium is an abundant dissolved cation in both seawater and hydrothermal fluids, with 97 seawater and Endeavour hydrothermal concentrations of ~87 µmol/kg and ~135 µmol/kg, 98 respectively (Butterfield et al., 1994; Seyfried et al., 2003; Turekian, 1968). With a similar ionic 99 charge and radius to Ba, Sr is a common trace substitution in barite. At the same time, both 100 seawater and hydrothermal fluid at Endeavour have very different, yet distinct Sr-isotope 101 (⁸⁷Sr/⁸⁶Sr) ratios. These ratios can be compared to the ratios measured in barite crystals, in 102 order to determine the relative proportion of seawater and hydrothermal fluid that make up 103 the fluid mixture from which barite precipitated. A similar approach has been used to 104 investigate the precipitation of anhydrite within the main active mound at the TAG 105 hydrothermal field on the Mid-Atlantic Ridge (Mills et al., 1998; Teagle et al., 1998) and the 21-106 Degrees North site on the East Pacific Rise (Albarede et al., 1981). However, there are few 107 reports of similar studies for hydrothermal barite (Kusakabe et al., 1990). In contrast to 108 anhydrite, which is unstable and will dissolve at ambient seafloor temperatures, barite has 109 extremely low solubility and behaves as a closed system under typical oxic seafloor conditions, 110 and is not prone to diagenetic alteration (Averyt and Paytan, 2003, and references therein; 111 Widanagamage et al., 2014). Barite can thus preserve geochemical and morphological features 112 associated with initial conditions of crystallization long after hydrothermal venting has ceased. 113 Barite is also the primary host in hydrothermal deposits for Ra, a radiogenic element that also 114 has a similar ionic charge and radius to Ba. The closed system behavior of barite also allows for the decay of ²²⁶Ra (half-life of 1,600 years) within the crystals to be used to determine absolute 115

ages of chimneys (de Ronde et al., 2005; Ditchburn et al., 2004; Ditchburn et al., 2012; Jamieson
et al., 2013).

118 In this study, we present data on the morphology, trace element distribution, Sr-isotope 119 composition and fluid inclusion analysis of barite collected from active and inactive 120 hydrothermal chimneys on the Endeavour Segment of the Juan de Fuca Ridge. The integrated 121 analysis of these multiple datasets provides constraints on the physical and chemical controls 122 associated with fluid mixing for barite precipitation within hydrothermal chimney walls. Results 123 of geochemical modeling are used to link the qualitative petrographic observations of barite 124 occurrence within the vent chimneys to the quantitative constraints on fluid mixing and the 125 physicochemical conditions of barite precipitation. This information can be used to infer the 126 formation temperatures and fluid chemistry of inactive chimneys, provide insights into the role 127 of fluid mixing within chimneys for the precipitation of other chimney-forming minerals, and 128 evaluate the locations of microbially-habitable zones within chimneys.

129 Geological Setting

The Endeavour Segment is a 90 km-long section of the Juan de Fuca mid-ocean ridge, which is
spreading at an average full-spreading rate of ~6 cm/yr (Fig. 1) (Goldstein et al., 1991;
Riddihough, 1984). The segment is bound to the south by the Cobb Offset and the Cobb
overlapping spreading center (OSC) and to the north by the Endeavour Offset and the
Endeavour OSC. The Cobb Offset represents a major geochemical division in the Juan de Fuca
Ridge, with normal mid-ocean ridge basalt (N-MORB) dominating the oceanic crust south of the
offset and enriched-MORB (E-MORB) dominating oceanic crust north of the offset (Karsten et

al., 1990). The occurrence of E-MORB at Endeavour has been attributed to a heterogeneous
mantle source of both enriched and depleted upper mantle with the enriched component of
the mantle source exhibiting enhanced melting relative to the depleted mantle source
(Cousens, 2010).

141 The Endeavour Segment ranges in depth from 2050 meters below sea level (mbsl) at a central 142 bathymetric high to >2700 mbsl towards the south end of the segment (Fig. 1) (Delaney et al., 143 1992). Active hydrothermal venting is focused within a 15 km-long central axial valley that 144 bisects the central volcanic high (Kelley et al., 2012). Within the axial valley are five major 145 hydrothermal vent fields (Sasquatch, Salty Dawg, High Rise, Main Endeavour Field, Mothra), 146 with several smaller vent fields and diffusely venting areas, making the Endeavour Segment one 147 of the most active hydrothermal areas on the mid-ocean ridge system (Fig. 1) (Kelley et al., 148 2012). Numerous inactive or extinct sulfide edifices occur on the axial valley floor outside of 149 the active vent fields (Clague et al., 2008; Jamieson et al., 2014). Hydrothermal activity has 150 been ongoing within the axial valley for at least the past ~3,000 years (Jamieson et al., 2013). 151 The sulfide edifices at Endeavour are typically steep-sided, often reaching heights of greater 152 than 20 metres above the seafloor, with fluid venting temperatures that range from <10°C up 153 to ~375°C (Butterfield et al., 1994; Delaney et al., 1992; Glickson et al., 2006; Kelley et al., 2012; Robigou et al., 1993). The edifices are unusually rich in barite, relative to other mid-ocean ridge 154 155 deposits. The high abundance of barite has been linked to the high Ba content of the 156 underlying E-MORB crust (Karsten et al., 1990; Tivey et al., 1999) and/or the presence of buried 157 sediments that have modified the chemistry of the hydrothermal fluids prior to venting

158 (Butterfield et al., 1994; Lilley et al., 1993; Proskurowski et al., 2004; Yao et al., 2009; You et al.,
159 1994).

Vent fluid chemistry within the Main Endeavour Field has been shown to be remarkably stable
from year to year (Butterfield et al., 1994). However, significant changes in fluid composition
over short periods have been linked to local seismic events (Seyfried et al., 2003). Factors such
as low chlorinity, relative to seawater, and short-lived venting of high-temperature, volatile-rich
fluids suggest that subsurface phase separation is an ongoing process (Butterfield et al., 1994;
Kelley et al., 2012; Larson et al., 2009).

166 Analytical Methods

167 Barite-rich samples for this study were collected from active and inactive hydrothermal 168 structures using remotely-operated vehicles (ROVs) and occupied submersible during several 169 research cruises to the Endeavour Segment between 1984 and 2011 (Delaney et al., 1992; 170 Glickson et al., 2006; Glickson et al., 2007; Jamieson et al., 2013; Kelley et al., 2012; Kelley et al., 171 2001; Kristall et al., 2006; Robigou et al., 1993; Tivey et al., 1999). Samples are generally fist-172 sized, and therefore their contained mineralogy and bulk chemistry may not reflect that of the 173 entire vent from which they were sampled. Thin sections and doubly-polished thick sections 174 $(80 \ \mu m)$ were prepared for petrographic and fluid inclusion analysis, respectively, by first 175 impregnating the samples in epoxy, due to their fragile nature, before cutting and polishing 176 each sample. Thin sections were examined using both reflected and transmitted light modes 177 with an Olympus BX 51 polarizing microscope with an attached Olympus DP71 digital camera.

Two samples – ALV2464-R4 and ALV2467-R2 – were selected for detailed analysis of barite
growth due to their large (>0.5 mm), euhedral zoned tabular barite crystals (Fig. 2). Sample
ALV2464-R4 is barite-rich and sulfur-poor, and was collected from the side of an old, Mn-coated
1.5 m tall, 1 m wide extinct spire within the High Rise vent field. ALV2467-R2 was collected
from a tall, thin extinct spire north of the Main Endeavour field.

183 *Geochemistry*

Concentrations of Ba, Ca and Sr within bulk samples were determined at ActLabs, in Ontario, Canada, using a combination of fusion inductively coupled mass spectrometry and instrumental neutron activation analysis (for Ba), and inductively-coupled plasma emission spectroscopy (for Ca and Sr). The reporting uncertainties are <10% over the range of measured concentrations.

188 Electron microprobe analysis

189 Concentrations of Sr, Ba, Ca and SO₄ within individual barite crystals were determined by 190 electron microprobe analysis (EMPA). Barites from seven carbon-coated thin-sections were 191 analyzed using an automated 4-spectrometer Cameca Camebax MBX electron microprobe at 192 Carleton University, using both energy-dispersive and wavelength-dispersive analytical modes, 193 with an accelerating voltage of 15 keV and a 20 nA beam current. Samples were selected in 194 order to maximize the variability in sample bulk Sr/Ba and barite crystal morphology. Analyses 195 for Fe, Cl, Cu and Zn returned concentrations below their respective analytical detection limits 196 (151 ppm, 31 ppm, 232 ppm, and 293 ppm, respectively).

197 Fluid Sr-isotope analysis

198 Thirty-one hydrothermal fluid samples for Sr isotope analysis were collected in 1995 and 2003 199 from high-temperature vents along the Endeavour segment using titanium syringe major 200 samplers and the Hydrothermal Fluid and Particle Sampler (Butterfield et al., 2004). Sub-201 samples for Sr isotope analysis were stored in acid-cleaned HDPE bottles and acidified with 202 ultra-pure HCl to pH <2. Strontium isotope compositions of fluids were analyzed by thermal 203 ionization mass spectrometry at the University of Washington with methods described by 204 Nelson (1995). Magnesium concentration was determined by ion chromatography (precision 205 1%). Strontium concentration in vent fluids was determined by atomic absorption 206 spectrophotometry (precision 4%).

207 Whole-rock Sr-isotope analysis

208 The bulk strontium isotope (87Sr/86Sr) composition of 16 barite-rich samples was determined 209 using thermal ionization mass spectrometry. For each analysis, approximately 50 mg of crushed 210 sample was leached in ~2 mL of 7M HNO3 on a 100°C hot plate in order to dissolve the sulfide minerals. This process was repeated three times in order to insure complete dissolution of 211 212 sulfides. The remaining barite crystals were immersed in 6M HCl and left covered on a 100°C 213 hot plate for three days. The solution was then removed by pipette and the samples were left 214 to dry down overnight. Finally, approximately 1.5 mL of 2.5M HCl was added to each solution 215 and the samples were left covered for two days. The solutions containing the dissolved barite 216 were run through Sr resin columns to isolate the Sr. The resulting samples were analyzed using 217 a ThermoFinnigan TRITON thermal ionization multi-collector mass spectrometer at Carleton

University. Samples underwent ~100 analyses at 1200-1406°C with a baseline measurement
taken after every 10 analyses.

220 In situ laser ablation analysis

221 Concentrations of a suite of 68 elements from Sr-rich and Sr-poor zones of a single crystal were 222 measured using a 193 nm Excimer laser ablation system coupled to a double-focusing, high-223 resolution magnetic sector AttoM (Nu Instruments) mass spectrometer at GEOMAR. Individual 224 analyses on the crystal surface consisted of continuous sampling along 100 µm rasters parallel 225 to the mineral zonation at a scan rate of 3 μ m/s, with a 32 μ m beam width and a fluence of 2 J/cm² at a repetition rate of 10 Hz. Ablation sites were chosen in order to avoid fractures or 226 227 areas with abundant fluid inclusions. External reproducibility of results was evaluated by 228 measurements of NIST612 and NIST610 glass standards and a synthetic sulfide standard 229 PGE Ni7b before and after barite analyses. For elements measured at two separate atomic masses (e.g., ^{33,34}S, ^{43,44}Ca and ^{135,137}Ba), the concentration measured using the more abundant 230 isotope (³⁴S, ⁴⁴Ca and ¹³⁷Ba) is used. 231

A New Wave UP193 laser, attached to an AXIOM multi-collector inductively-coupled plasma mass spectrometer, also at GEOMAR, was used to measure the ⁸⁷Sr/⁸⁶Sr composition of individual zones within single barite crystals from two samples, including the same crystal analyzed for trace element abundances. Analyses and data reduction using a LRS (linear regression slope) method followed the approach described by Fietzke et al. (2008).

Single analyses on the crystal surfaces consisted of 100 μ m line scan ablations parallel to the Sr zonation using a spot size of 25 μ m, fluence of 2 J/cm² and repetition rate of 10 Hz at a 3 μ m/s

- scan speed. Precision and accuracy of the measurements was evaluated by repeat duplicate
- analysis of a modern marine carbonate reference standard after every fifth analysis. See
- supplementary information for further analytical details.

242 Microthermometry

- 243 For microthermometry measurements, samples were prepared as ~50 μm-thick doubly
- polished sections mounted with acetone-soluble glue. Samples were removed from the carrier
- glass using acetone prior to microthermometry measurements. Due to the excellent cleavage of
- barite, care was taken so that only pristine fluid inclusions distal to internal fractures were
- selected. Measurements were made using Linkam[®] THMS 600 heating-freezing stages at
- 248 GEOMAR and at the Department of Geosciences, University of Kiel. Each apparatus was
- 249 mounted on a standard petrographic microscope with long working distance optics.
- 250 The heating-freezing stages were calibrated using SYNFLINC[®] synthetic fluid inclusion
- 251 temperature standards. Accuracy and precision were estimated at ± 0.2 °C near the triple point
- of CO₂ (\pm 56.6 °C), and better than \pm 0.5 °C at other temperatures below ambient. Accuracy and
- 253 precision for total homogenization measurements were estimated at ± 2 °C.
- 254 Salinities were calculated using the following equation from Bodnar and Vityk (1994):

255 Salinity (wt.%) =
$$-1.78(T_m) + 0.0442(T_m)^2 - 0.000557(T_m)^3$$
 (1)

where T_m is the final melting temperature, in degrees Celsius, of the solid phase within the
 inclusion upon heating from below the freezing point. Formation, or trapping temperatures (T_t)
 were determined by applying a hydrostatic pressure correction to the homogenization

259	temperatures (T _h), which is defined as the minimum temperature in which a single phase fluid is
260	present in the inclusion. For pressure corrections, isochores were calculated using the FLUIDS
261	software package (Bakker, 2003; Bakker, 2012).
262	Cooshamical Modeling
202	Geochemical Wodeling
263	Concentrations of free barium, strontium, calcium and sulfate, and saturation states of barite,
264	anhydrite and amorphous silica, were determined as a function of temperature assuming
265	mixing of 350°C vent fluid and seawater (Table 1). Calculations were made using the modeling
266	code EQ3/6 (Wolery, 1992; Wolery and Daveler, 1992) with mineral precipitation and

- $\label{eq:267} equilibrium between \ H_2S-SO_4 \ and \ CO_2-CH_4 \ suppressed. \ Thermodynamic \ data \ used \ were \ from$
- SUPCRT92 (Johnson et al., 1992), with data for MgSO₄ and NaSO₄⁻ species added (McCollom and
- 269 Shock, 1997).

270 Results

271 Crystal Morphology

272 Barite within hydrothermal vents at Endeavour occurs as a wide range of crystal habits, from 273 well-formed tabular and bladed crystals to dendritic crystals (Fig. 3). The majority of samples 274 contain barite that is not restricted to a single crystal morphology and crystals with different 275 habits often occur in different areas of a single sample. However, samples can be grouped into 276 four broad morphological categories defined by the dominant morphologies present: 1) wellformed, tabular crystals (Fig. 3A); 2) bladed crystals (Fig. 3B); 3) acicular and/or radiating 277 278 tapered crystals (Fig. 3C); and 4) dendritic crystals (Fig. 3D). Barite crystals vary in size from <0.1 279 mm up to 2 mm, and the larger crystals tend to have a more euhedral (tabular or bladed)

280 morphology. Sphalerite and pyrite are the most common sulfide minerals present in barite-rich 281 samples. Sphalerite is the dominant sulfide phase in samples with tabular or bladed barite, 282 whereas pyrite is more common in samples that contain smaller acicular or dendritic barite. 283 Barite typically crystallizes into open pore spaces, precipitating on pre-existing sulfide minerals, 284 with the exception of dendritic barite, which often occurs as outward-facing fans on the 285 exterior of a sample (Fig. 3D). Amorphous silica is generally the only phase that precipitates 286 after barite and can be seen coating barite crystals in some samples, although sulfide 287 overgrowth or replacement of relict barite is also present.

288 Trace element content of barite

289 Whole rock Ba and Ca concentrations for 335 chimney samples are plotted in Figure 4A (see 290 Supplementary Table S1 for full results). The Ba and Ca concentrations reflect the amount of 291 barite and anhydrite in each sample, respectively, and range from below detection limits up to 292 \sim 40 wt. % for both elements. The strong negative correlation between Ba and Ca is typical of 293 hydrothermal vents in this and other locations (Hannington et al., 1995; Koski et al., 1994), and 294 reflects the different saturation conditions under which barite and anhydrite precipitate within 295 vents. The whole rock Sr concentrations are plotted against Ba in Figure 4B. The samples are 296 divided into those with either greater than or less than 1 wt. % Ca. For samples with less than 1 297 wt. % Ca, Sr concentrations range from 0 to 1.3 wt. % and there is a positive correlation 298 between Sr and Ba (R² = 0.74). Samples that contain more than 1 wt. % Ca are generally Ba-299 poor, and contain up to only ~0.3 wt. % Sr, but show a similarly strong positive correlation 300 between Ca and Sr ($R^2 = 0.83$). The strong correlations between Sr and both Ba and Ca indicate 301 that barite and anhydrite are the primary mineral phases that host Sr in hydrothermal chimneys 302 at Endeavour. Because Ba-rich samples are generally Ca-poor, bulk of the Sr within Ba-rich 303 samples will be contained within barite, and thus the reported whole rock ⁸⁷Sr/⁸⁶Sr ratios for 304 Ba-rich samples represents the Sr isotopic composition of barite within these samples.

305 Electron microprobe analysis of growth zones within individual barite crystals indicate that Sr 306 and Ca are the major trace elements within barite and that the darker chemical zonations 307 visible in the backscatter images reflect higher concentrations of Sr and Ca within the crystals 308 (Fig. 5A and B). Strontium content (reported as percent relative to total Ba+Sr+Ca) ranges from 309 0% to 18%, with an average of 5.5% from 41 analyses. Calcium values are lower, and range 310 from 0% to 10.9% and averages 1.9% (n = 35) (see Supplementary Table S2 and Figure S1 for full 311 results).

312 Trace element concentrations from laser ablation analysis of a single barite crystal from

313 ALV2467-R2 is reported in Table 2 (lines A through H in Fig. 5C). Although concentrations of 68

314 elements were measured, only the elements with concentrations above detection limits are

315 reported (see Supplementary Table S3 for results for all elements). The results are similar to

316 the electron microprobe results, and indicate that concentrations of all measured trace

317 elements (Sr, Ca and K) are higher within the darker zones.

318 Hydrothermal fluid Sr concentrations and ⁸⁷Sr/⁸⁶Sr composition

319 The zero Mg endmember Sr isotope composition for vent fluids is determined by linear

regression of ⁸⁷Sr/⁸⁶Sr ratio with Mg/Sr ratio and extrapolation to zero Mg/Sr (Butterfield et al., 320

2001). There is minor variation in the ⁸⁷Sr/⁸⁶Sr endmember between vent fields along the axis. 321

322 When all samples are regressed together, the composite endmember for the whole segment is

323 0.70343 ± 0.00015. The majority of fluid samples were taken in the Main Endeavour Field 324 (MEF), potentially biasing the results of the composite regression. When the endmember for 325 each vent field is regressed independently, and then vent field endmembers averaged for the 326 segment, a similar value of 0.70343 ± 0.00011 is obtained. This value is within the uncertainty range of the average ⁸⁷Sr/⁸⁶Sr value of 0.70329 ± 0.00037 (1-sigma) for hydrothermal fluids 327 328 from mid-ocean ridge-hosted hydrothermal systems, based on measurements from the East 329 Pacific Rise (Von Damm, 1990) and Mid-Atlantic Ridge (Elderfield et al., 1993; Gamo et al., 1996; 330 James et al., 1995; Von Damm, 1990)

Endmember Sr concentrations generally vary with vent fluid chloride concentration (Seyfried et al., 2003). Taking the average Sr concentrations of the endmembers for individual fields (using the same samples used for the Sr isotopic endmember) yields an average Sr concentration of $163 \pm 52 \mu mol/kg$.

335 Whole rock ⁸⁷Sr/⁸⁶Sr compositions

Whole rock Sr-isotope (⁸⁷Sr/⁸⁶Sr) ratios for 16 chimney samples are reported in Table 3. Ratios
range from 0.703798 to 0.707581 and all fall between the values for Endeavour vent fluids
(0.7033) and modern seawater (0.709183) (Butterfield et al., 2001). Lower ⁸⁷Sr/⁸⁶Sr ratios were
generally found in samples dominated by dendritic and acicular barite crystals, whereas higher
ratios were typical of samples containing dominantly well-formed, tabular crystals.

341 ⁸⁷Sr/⁸⁶Sr variations within barite crystals

- 342 Results of laser ablation analysis of discrete zones along single barite crystals in samples
- 343 ALV2464-R4 and ALV2467-R2 are reported in Table 4 and plotted in Figure 6 (locations of

analyses are shown in Fig. 5D). For both crystals, there is a clear association between darker
zones visible in the backscatter images and higher concentrations of Sr (open blue ovals),
similar to the results from electron microprobe analyses.

For ALV2464-R4, ⁸⁷Sr/⁸⁶Sr values along the crystal are, with the exception of lines 16 and 21, 347 348 within error of each other, and cluster around a value of 0.7046 (green dashed line) which represents the whole rock ⁸⁷Sr/⁸⁶Sr value for this sample (Table 3). Analyses #16 and #21 both 349 350 sampled fluid inclusion-rich zones within the crystal (appear as dark pits in the backscatter image in Fig. 6). The ⁸⁷Sr/⁸⁶Sr values for these samples are higher than those for the rest of the 351 352 crystal, suggesting that the inclusions may contain fluids that have a higher proportion of 353 seawater, relative to the surrounding crystal. There is a very weak negative correlation 354 between Sr abundance in the crystal (measured as Sr-intensity) and ⁸⁷Sr/⁸⁶Sr values (Fig. 7). 355 However, if analyses #16 and #21 are excluded, there is essentially no systematic variation in ⁸⁷Sr/⁸⁶Sr with Sr abundance in the crystal. 356

For ALV2467-R2, there is a smaller range in ⁸⁷Sr/⁸⁶Sr values than ALV2464-R4, and the values cluster near the whole-rock value of 0.7038 (Fig. 6). A negative correlation between ⁸⁷Sr/⁸⁶Sr values and Sr concentration is slightly more pronounced for this sample (Fig. 7), suggesting that the partitioning of Sr into the barite lattice is greater when the source fluid has a higher proportion of hydrothermally-derived Sr.

362 *Microthermometry*

Fluid inclusions were investigated in barite and in interstitial amorphous silica from samples
 ALV2464-R4 and ALV2467-R2. These samples contain both liquid-dominated and vapour-

365 dominated 2-phase liquid (L) + vapour (V) inclusions at ambient temperatures (Fig. 8). In rare 366 cases, metastable single-phase L inclusions that nucleated a vapour bubble upon cooling below 367 room temperature were encountered. The overall size of individual fluid inclusions ranges from 368 <1 μ m to ~30 μ m. However, only inclusions between 2 and 10 μ m were subject to 369 microthermometry measurements.

370 Fluid inclusions within the barite crystals can be texturally classified as either primary or 371 secondary. Primary inclusions occur either as solitary inclusions or small clusters that are well 372 removed from grain boundaries, or as trails within growth zones of the host mineral (Fig. 8A 373 and B). Secondary fluid inclusions occur as trails in healed cracks crosscutting growth zones (if 374 applicable) and ending at the surface boundary of the respective crystal (Fig. 8C). Rare primary 375 fluid inclusions also occur in the interstitial amorphous silica (Fig. 8D). The terms "primary" and 376 "secondary" inclusions as used here apply to single crystals (and in rare cases to their 377 immediate surroundings), and thus do not necessarily imply that all primary inclusions in a 378 given sample were formed earlier than secondary inclusions.

Within each sample, most primary fluid inclusions and many of the secondary inclusions are
liquid dominated (i.e. they have vapour bubble sizes comprising less than ~30% of the inclusion
volume). A sub-set of secondary inclusions form trails that include vapour-dominated
inclusions as well. However, careful microscopic investigations indicate that neighbouring
liquid-dominated fluid inclusions within many growth zones and secondary trails have variable
L/V phase proportions, which is a strong indication of post-entrapment modification upon
cooling, involving progressive crack healing, or necking down, after initial bubble formation of

the host mineral (Roedder, 1984). Therefore, only inclusion trails where neighbouring inclusions
have similar L/V phase proportions, and were therefore assumed to represent the original
densities, were selected for microthermometry measurements.

389 Upon cooling, the fluid inclusions froze to aggregates of ice and vapour at temperatures 390 between -35 and -55 °C. Once frozen, the vapour bubbles within inclusions containing a vapour 391 phase of less than about 10 vol. % were squeezed out of existence due to expansion of the 392 aqueous phase during the water to ice transition. Further cooling to about -70 to -110 °C 393 produced no further phase changes, implying that gaseous species such as CO₂ or CH₄ can only 394 be present in amounts less than about 5 mole %, if at all (Konnerup-Madsen, 1995). Upon 395 heating the inclusions, initial melting (T_i) occurred between -35 to -21 °C, which is close to the 396 eutectic point in a NaCl-H₂O-dominated system. Final melting temperatures (T_m) ranged 397 between –5.4 to -3.5 °C. Using equation (1), final melting temperatures correspond to an 398 average salinity of 7.6 \pm 1.1 wt. % NaCl equivalent (1-sigma, n = 8) for ALV2464-R4 and 6.6 \pm 1.2 399 wt. % NaCl equivalent (1-sigma, n = 2) for ALV2467-R2 (Table 5). A final melting temperature of 400 -2.0 °C from a single inclusion within amorphous silica from ALV2464-R4 corresponds to a NaCl 401 equivalent salinity of 3.4 wt. %, which is near seawater values (Bakker, 2012; Bodnar and Vityk, 402 1994).

Final homogenization temperatures of liquid + vapour (L + V) into liquid occur at temperatures
between 114 and 269 °C for inclusions within barite (n=64), and 118 to 127 °C for inclusions
within amorphous silica (n=5) (see Supplementary Table S5 for full results). Sample water
depths of about 2,200 m corresponds to a pressure of 22 MPa (220 bar), and translates into

pressure corrections of 10 to 14 °C and corrected formation temperatures of 124 to 283 °C and
128-137 °C for barite- and amorphous silica-hosted inclusions, respectively (Fig. 9). The highest
formation temperatures in both samples correspond to primary inclusions within large, blocky
(euhedral) crystals. Lower formation temperatures are associated with secondary liquid
dominated inclusions.

412 Discussion

413 Fluid inclusions

414 Primary fluid inclusions allow for the direct determination of fluid temperature and salinity 415 during barite precipitation whereas secondary inclusions record post-crystallization events. The 416 primary inclusions in the analyzed samples are liquid-dominated, indicating barite precipitation 417 from a vapour-poor fluid, and occur mainly within larger, euhedral barite crystals. Trapping 418 temperatures of the majority of the primary inclusions indicate barite formation temperatures 419 of between 180 and 240°C (Fig. 9). The highest measured trapping temperatures may be a 420 result of necking down effects on the inclusions. These temperatures are consistent with 421 previously reported temperatures for barite precipitation (e.g., Halbach et al., 1989; 422 Hannington et al., 1995; Hannington and Scott, 1988). 423 Secondary fluid inclusions are both liquid- and vapour-dominated, indicating later stage vapour-424 rich venting. Formation temperatures for secondary inclusions are lower than those for 425 primary inclusions, and cluster between $\sim 130 - 150$ °C. Secondary inclusions are also typically 426 found in smaller, less well-formed crystals, which is consistent with results of geochemical 427 modelling that links less well-formed crystals to higher degrees of fluid supersaturation at lower

temperatures (see discussion on crystal morphology below). Direct venting of a vapour phase
has been reported at Endeavour; however these venting events have been short-lived events
associated with episodes of venting of fluids with temperatures at or above the seawater
boiling curve (Butterfield et al., 1994; Kelley et al., 2012; Seyfried et al., 2003).

432 Measured fluid salinities from primary inclusions in barite from samples ALV2467-R2 and 433 ALV2464-R4 are above that of seawater, suggesting that the vent fluid contained a component 434 of a brine phase during barite formation for both samples (Coumou et al., 2009). Using the % hydrothermal fluids determined using bulk ⁸⁷Sr/⁸⁶Sr (summarized in Table 3), and a seawater 435 436 salinity of 3.3 wt. %, the average salinity of 7.6 wt. % NaCl equivalent from sample ALV2464-R4 437 corresponds to a hydrothermal fluid with a salinity of 9.4 wt.%. For ALV2467-R2, the calculated 438 hydrothermal fluid salinity is 7.1 wt.%. Phase separation is generally accepted to be an 439 important control on fluid chemistry at MEF and High Rise; however, so far only venting of low-440 salinity fluids has provided any direct evidence of phase separation in the subsurface at these 441 sites (Butterfield et al., 1994; Kelley et al., 2012; Seyfried et al., 2003). Venting of a high-salinity fluid has not been documented at MEF or High Rise, and the presence of a brine layer in the 442 443 subsurface is only predicted from mass-balance constraints (Seyfried et al., 2003). The high-444 salinity fluid inclusions presented here may be the first evidence of past venting of a brine component at MEF and High Rise. 445

The fluid inclusion temperature and salinity data indicate an early stage of higher-temperature
barite precipitation from a vapour-poor, high-salinity fluid, followed by later-stage lower
temperature venting of a vapour-rich fluid. The occurrence of high vapour content is at odds

449 with lower inclusion formation temperatures. However, it should be noted that the fluid 450 inclusions are recording the local conditions within the chimney walls where significant mixing 451 with seawater and/or conductive cooling may have resulted in the cooling of otherwise high-452 temperature endmember vent fluid. 453 Formation temperatures of 120 – 140°C for amorphous silica are consistent with previous 454 estimates by Tivey et al. (1986) and, along with measured fluid salinity near that of seawater, 455 are consistent with precipitation towards the exterior of the chimney walls. 456 Fluid Mixing

The measured ⁸⁷Sr/⁸⁶Sr values within hydrothermal barite in this study (both whole rock and laser ablation spot analyses) lie between the endmember values for seawater and Endeavour hydrothermal fluid (Table 1), and record the amount of mixing between these two endmember fluids at the sites of barite precipitation within vent chimney walls. The relative contribution of each endmember fluid can be quantified by applying a two component mixing model:

462
$$[Sr]_{SW} \left[{\binom{87}{Sr}} Sr_{86} Sr \right]_{SW} - {\binom{87}{Sr}} Sr_{86} Sr \right]_{BA} \right] + [Sr]_{HF} \left[{\binom{87}{Sr}} Sr_{86} Sr \right]_{HF} \right]$$
(2)

where %*HF* is the proportion of hydrothermal fluid (with the remaining proportion being
seawater), [*Sr*]_{*SW*} and [*Sr*]_{*HF*} are the Sr concentrations of seawater and the hydrothermal fluid,
respectively, and (⁸⁷Sr/⁸⁶Sr)_{SW}, (⁸⁷Sr/⁸⁶Sr)_{HF} and (⁸⁷Sr/⁸⁶Sr)_{BA} are the Sr-isotope ratios for
seawater, hydrothermal fluid and barite, respectively (Mills et al., 1998). This model assumes
that there is no fractionation of Sr isotopes during precipitation of barite. An investigation by

Widanagamage et al. (2014) of Sr-isotope fractionation during synthetic barite precipitation at
temperatures of up to 40°C indicated a maximum fractionation (difference in ⁸⁷Sr/⁸⁶Sr between
barite and solution) of ~0.0002, which is equivalent to or less than the analytical uncertainty of
the measurements presented in this study (Tables 3 and 4). Fractionation factors for barite
precipitation in hydrothermal chimneys would likely be much smaller than those reported by
Widanagamage et al., due to higher temperatures.

The relative contributions of each endmember fluid that resulted in barite precipitation, based on equation (2), varies from 17 to 88% hydrothermal fluid, and averages 62% (Table 1). For comparison, Kusakabe et al. (1990) report hydrothermal contributions of between 80 and 90% for hydrothermal barite from the Mariana backarc basin using a similar approach. The relative contributions of each endmember fluid can be combined with the physical and chemical properties of the endmember fluids to infer the physical and chemical conditions under which barite precipitated within the chimney walls.

481 *Temperature*

The fluid temperature within a chimney wall is dependent on the combined effects of the amount of mixing between hot hydrothermal fluid and cold seawater and conductive cooling of the hydrothermal fluid or heating of seawater. If considering only the temperature effects of fluid mixing, the temperature at which barite precipitates can be inferred using a linear thermal mixing relationship:

487
$$T = X(T_{HF}-T_{SW}) + T_{SW}$$
 (3)

where T is the temperature of the mixed fluid in degrees Celsius, T_{HF} and T_{SW} are the 488 489 temperatures of endmember hydrothermal fluid and seawater, respectively, also in degrees 490 Celsius (Table 1), and X is the fraction of hydrothermal fluid in the mixture, calculated using 491 equation (2) (Fig. 10) (Mills and Elderfield, 1995). The endmember hydrothermal fluid 492 temperature of 350°C represents average typical maximum vent fluid temperatures at 493 Endeavour (Kelley et al., 2012; Seyfried et al., 2003). Temperatures of up to 375°C have been 494 recorded at MEF, and represent the thermodynamic maximum temperature of seawater 495 defined by the hydrostatic pressure at that depth (220 bars at 2,200 m), suggesting that these 496 fluids are on the liquid-vapour phase boundary for seawater (Bischoff and Rosenbauer, 1985; 497 Delaney et al., 1992; Kelley et al., 2012; Tivey et al., 1990). A short-lived episode of higher fluid 498 temperatures (>400°C) has been reported for the Main Endeavour Field, and is thought to 499 represent a brief period of venting of a vapour phase (Butterfield et al., 1994; Tivey et al., 500 1990).

Calculated mixing temperatures using equation (3) range from 61 to 308 °C for 16 samples from
the Endeavour Segment (Table 3). These values are comparable to previous estimates of the
temperature range under which hydrothermal barite typically precipitates on the seafloor (e.g.,
~100 – 300 °C) (Blount, 1977; Hannington et al., 1995).

For samples ALV2464-R4 and ALV2467-R2, the barite formation temperatures based on fluid
inclusion microthermometry are lower than the predicted temperatures from fluid mixing by 56
and 119 °C, respectively. Conductive cooling within the chimney walls will result in fluid
temperatures being lower than the value calculated based purely on fluid mixing (Hannington

and Scott, 1988; Tivey and Delaney, 1986). If the microthermometry results are considered to represent the true temperatures of barite precipitation, the temperature difference between the two methods represents the amount of conductive cooling of the hydrothermal fluid within the chimney walls. Hannington and Scott (1988) estimate a decrease in fluid temperature of 75°C (from 350°C to ~275°C) from conductive cooling, followed by mixing with 50% seawater, allows for the co-precipitation of barite and silica at 185°C within the wall of a hydrothermal spire from Axial Seamount, which is also on the Juan de Fuca Ridge.

516 Barite Precipitation

517 Geochemical modelling of the mixing between Endeavour hydrothermal fluid and seawater 518 allows for the evaluation of the saturation state of the mixed fluid with respect to barite (and 519 other minerals) at different stages of mixing, by accounting for the combined effects of 520 temperature, fluid composition and chemical speciation (Fig. 10). Figure 10A shows variation in the total concentrations of free- and total-dissolved Ba²⁺, Sr²⁺, and SO₄²⁻ as a function of both 521 522 temperature and degree of mixing, using fluid properties summarized in Table 1. The 523 concentrations of free species represents the amount of solute available for mineral 524 precipitation. For Ba, Ba²⁺ is the dominant species in the mixed fluid, especially at lower 525 temperatures. At temperatures above ~200°C, the relative abundance of BaCl⁺ increases and 526 the absolute concentration of Ba²⁺ begins to decrease, even though the total Ba in the fluid 527 increases towards higher temperatures. Strontium follows a similar pattern, although, unlike 528 Ba, higher concentrations of Sr are maintained at lower temperatures due to the relatively high 529 abundance of dissolved Sr in seawater. The high concentration of SO₄²⁻ at low temperatures 530 reflects the relatively high concentrations of sulfate in seawater and negligible sulfate in the

531 hydrothermal fluid. However, the slightly irregular surface of the concentration profile in 532 Figure 10A is a result of the complex speciation of sulfate, involving several different cations 533 (Fig. 10B). In particular, the sudden dip in SO_4^{2-} concentration at ~100°C is associated with a 534 sudden increase in NaSO₄²⁻.

535 The physicochemical conditions for precipitation or dissolution of barite can be quantified by 536 determining the saturation index of the fluid (S.I. = log Q/K, where Q is the activity product and 537 K is the equilibrium constant). An S.I. > 0 will result in mineral precipitation, and a S.I. < 0 will 538 result in mineral dissolution. Saturation indices for barite, anhydrite and amorphous silica are 539 plotted in Figure 10C. According to the model, barite will precipitate from mixing fluid 540 temperatures of between ~5 and 330°C. These temperatures correspond to fluid mixtures that 541 contain as little as 1% hydrothermal fluid, and as much as 94% hydrothermal fluid, reflecting 542 the very low solubility of barite. Anhydrite will precipitate from the fluid at mixing 543 temperatures greater than ~120°C. The model predicts that amorphous silica, which is often 544 abundant within Endeavour hydrothermal vents (e.g., Fig 2A) will never reach saturation and will not precipitate purely as a result of fluid mixing. However, as noted above, the mixing 545 546 model does not consider conductive cooling, which is required for precipitation of amorphous 547 silica (Tivey and Delaney, 1986).

548 The modeling results presented in Figure 10 also do not consider the effects of mineral 549 precipitation on fluid composition and saturation index. Because of the high degree of 550 supersaturation of anhydrite relative to barite at high temperatures (Fig. 10C), anhydrite 551 precipitation would remove sulfate from the solution, inhibiting the precipitation of barite at

these high temperatures, resulting in the typical association of anhydrite with high-temperature
sulfide minerals (e.g., chalcopyrite, pyrrhotite) in the interior, and barite with lower
temperature sulfide minerals (pyrite, sphalerite) towards the exterior of a chimney (Hannington
et al., 1995).

556 The hydrothermal fluid Ba concentration reported in Table 1 represents the maximum reported 557 non-endmember value for the Main Endeavour Field. Because of its very low solubility, 558 precipitation of barite reduces the amount of dissolved Ba during fluid sampling, and results in 559 non-linear behavior when determining zero-Mg endmember values and, for this reason, 560 endmember Ba concentrations are rarely reported (Seyfried et al., 2003). The concentration of 561 Ba within Endeavour hydrothermal fluid is likely higher than the maximum reported value of 31 562 μ mol/L (Seyfried et al., 2003), and endmember Ba concentrations could easily be twice this 563 amount. Reported endmember Ba concentrations at Lucky Strike, another E-MORB-hosted 564 hydrothermal site, are comparable and range between 10 and 52 μ mol/L (Charlou et al., 2000). 565 However, in this case the authors also state that the reported concentrations likely represent 566 minimum values. The highest reported endmember Ba concentration for a vent fluid is 119 567 µmol/L, from fluids sampled from the Edmond site, on the Central Indian Ridge (Kumagai et al., 568 2008). The high values at this site are also attributed to enriched Ba within the underlying 569 source rocks. Whether or not this maximum reported concentration is representative of the 570 actual endmember concentration is unclear. However, this value does point to the possibility 571 of hydrothermal fluid Ba concentrations at Endeavour (and other mid-ocean ridge 572 hydrothermal sites) to be significantly higher than the non-endmember values reported for 573 Endeavour fluids. For this reason, Figure 10C also includes the saturation index for barite using

double the amount of dissolved Ba (i.e., 62 µmol/Kg). The increased Ba concentration results in
a nearly constant offset to higher S.I. values, but otherwise the conditions under which barite
precipitates remain relatively unchanged.

577 The similar shapes of the two barite curves in Figure 10C, and their roughly similar shape to the Ba²⁺ concentration profile in Figure 10A suggest that Ba is the limiting reagent during barite 578 579 precipitation, and the fluid mixture contains an excess of sulfate. The stoichiometric relationship between Ba^{2+} and SO_4^{2-} in barite is such that, ignoring trace substitutions, equal 580 581 molar amounts of each constituent are consumed from the mineralizing fluid during 582 crystallization. Using the fluid parameters outlined in Table 1 and the mixing model defined by equation 2, equal moles of Ba^{2+} and SO_4^{2-} in a mineralizing fluid (the intersection of the Ba^{2+} and 583 SO₄²⁻ curves in Fig. 10A) would require a greater than 99% hydrothermal fluid component, due 584 585 to the much higher sulfate concentrations in seawater, relative to the hydrothermal fluids at 586 Endeavour. As noted in Table 3, barite samples from Endeavour precipitated from fluid 587 mixtures containing significantly less than 99% hydrothermal fluid, confirming that sulfate is in 588 excess and Ba²⁺ availability is the dominant control on barite precipitation.

589 Crystal Morphology

Laboratory growth experiments have linked barite crystal morphology to crystal growth rates and the degree of supersaturation of Ba²⁺ and SO₄²⁻ in the crystallizing fluid (Judat and Kind, 2004; Li et al., 2007; Shikazono, 1994; Widanagamage et al., 2014). Dendritic crystals grow quickly as a result of diffusion-limited aggregation of solute atoms from highly supersaturated fluids (Turcotte, 1997). Well-formed crystals grow more slowly at lower degrees of

supersaturation, predominantly from surface reaction precipitation mechanisms (Shikazono,1994).

597 A comparison of dominant barite crystal morphology for samples from Endeavour to degree of 598 fluid mixing and S.I. (Fig. 10C; Table 3) shows a relationship consistent with the experimental 599 results described above. A marked increase in S.I. occurs at temperatures between ~10 and 140°C, which corresponds to an increase in SO₄²⁻ concentration that coincides with a marked 600 601 decrease in the stability of NaSO₄⁻. The single sample that plots in this region (ALV1452-1A) 602 contains mainly dendritic barite, which is in generally agreement with the experimental results 603 of Shikazono (1994), although the magnitude of supersaturation is significantly less, likely a 604 result of highly dynamic fluid environment within a vent chimney wall, compared to static 605 laboratory experiments. Shikazono (1994) demonstrated that, under static laboratory 606 conditions of 150°C and pressures equal to the vapour pressures of the aqueous solutions, 607 barite that precipitates from a solution with an S.I. below 20 will form well-formed barite 608 crystals. Dendritic crystals will form from a solution with an S.I. larger than 20 (i.e. a higher degree of supersaturation). The results from this study suggest that, in the dynamic 609 610 environment within vent chimney walls, dendritic barite forms at low temperatures and high 611 inputs of seawater, resulting in a S.I. of above ~0.6. This relationship is consistent with the 612 typical occurrence of dendritic barite along the outer margins of a vent (e.g., Fig. 3D).

613 Strontium partitioning

614 The degree of Sr substitution in barite, expressed as an apparent partition coefficient (K_D = 615 (Sr/Ba)_{barite}/(Sr/Ba)_{fluid}), was calculated for individual samples using whole rock geochemical

616 data and modelled fluid compositions (Table 3). Calculated K_D values are reported as 617 "apparent" values because the rapid temperature changes and high fluid flow velocities 618 associated with hydrothermal venting, as well as the occurrence of dendritic crystal 619 morphologies associated with high degrees of supersaturation, indicate non-equilibrium 620 conditions during barite crystallization (Shikazono, 1994). Trace element substitution within 621 crystals is controlled by the composition of the crystallizing fluid, pressure, temperature and 622 crystal growth rate (Averyt and Paytan, 2003; Hannington and Scott, 1988; Sasaki and Minato, 623 1983). However, the effects of these external factors on element partitioning within barite 624 under hydrothermal conditions are not well constrained (Shikazono et al., 2012). Laboratory 625 experiments and thermodynamic constraints for typical marine conditions (i.e. low-626 temperature) indicate that Sr substitution in barite increases with temperature (Averyt and 627 Paytan, 2003; Hanor, 2000). Alternatively, under hydrothermal conditions, Shikazono et al. 628 (2012) link increased Sr partitioning to higher degrees of supersaturation and fast crystal 629 growth, which, in this case, occur at lower temperatures. Sasaki and Minato (1983) suggest 630 that, from precipitation experiments at temperatures between ~25 - 60°C, the degree of 631 supersaturation has a stronger control on Sr partitioning than temperature. A comparison of 632 Sr/Ba ratios to degree of fluid mixing from this study indicates a weak relationship of increased 633 Sr substitution with lower proportions of hydrothermal fluid contribution (Fig. 11A). However, 634 a plot of the same data against apparent partition coefficient, which takes into account the 635 Sr/Ba of the modelled fluid as that of the barite crystals shows no relationship between degree 636 of mixing and Sr substitution, indicating that different degrees of mixing, and hence fluid 637 composition, is not a primary control on Sr substitution (Fig. 11B).

Apparent partition coefficients for individual Sr-rich and Sr-poor zones within a single crystal 638 639 were also determined using crystal chemistry derived from laser ablation (Table 2) and modeled fluid compositions (Table 6; Fig. 11B). The consistent ⁸⁷Sr/⁸⁶Sr across individual Sr-rich 640 641 and Sr-poor growth zones (Fig. 6) provide further evidence that Sr partitioning in the barite is 642 not controlled by fluid mixing. The pattern of Ca substitution mimics that of Sr, which suggests 643 that the zonation is not a result solely of temporal variations in fluid Sr concentrations either. 644 Furthermore, Butterfield et al. (1994) report remarkably stable vent fluid chemistry at MEF over 645 a 4-year period. The higher abundance of fluid inclusions within the darker growth zones 646 suggests that higher degrees of Sr substitution reflect periods of faster crystal growth, driven by 647 increased conductive cooling that results in a higher degree of supersaturation. Changes in the 648 amount of conductive cooling could result from oscillations in hydrothermal fluid flux. Without 649 information on crystal growth rates, it is difficult to evaluate how much time is represented by 650 each growth zone. However, the sharp boundaries between zones and oscillatory nature of the 651 zonations suggest that the environmental factor(s) responsible for the zonations occur quickly 652 and cyclically. Common necking-down of fluid inclusions also points to temperature oscillations 653 during barite growth. The lighter zones are generally larger than the darker zones. This, 654 coupled with the fact that crystal growth is likely faster during formation of the darker zones, 655 indicates that conditions that favour lower levels of Sr substitution (i.e. the lighter zones; Fig 656 5B) during crystal growth occur over longer periods of time than conditions that favour higher 657 levels of Sr substitution.

658 Conclusions

659 The investigation of barite within hydrothermal vents along the Endeavour Segment of the Juan 660 de Fuca Ridge provides insights into the physical and chemical conditions associated with the 661 mixing of hydrothermal fluid and seawater within the porous vent chimney walls. A twocomponent mixing model based on ⁸⁷Sr/⁸⁶Sr compositions indicates that , due to the very low 662 663 solubility of barite, precipitation can occur at almost any proportion of mixing of the two fluids, with barite from Endeavour containing ⁸⁷Sr/⁸⁶Sr that indicate as little as a 17% hydrothermal 664 665 fluid component and as much as an 88% hydrothermal fluid component. Barite can thus 666 precipitate at any stage during the growth history of a hydrothermal vent. Precipitation of 667 barite from mixtures containing greater than 50% hydrothermal fluid may be inhibited by SO_4^{2-} 668 removal from the fluid resulting from anhydrite precipitation. 669 The degree of fluid supersaturation with respect to barite is controlled largely by the availability 670 of free Ba²⁺ in the fluid mixture. High degrees of supersaturation associated with higher 671 proportions of seawater result in the precipitation of barite dominated by acicular and dendritic 672 morphologies, whereas large, tabular and bladed crystals occur in more Ba-limited conditions in 673 the interior regions of chimneys.

674 Cyclical Sr zonations within single barite crystals result from changes in crystal growth rates that
675 are likely associated with temperature minor temperature fluctuations during venting, and not
676 changes in fluid chemistry or degree of fluid mixing.

677 Results from fluid inclusion microthermometry indicate that the more euhedral crystals form at
678 temperatures between ~120 and 240°C, which is consistent with previous estimates for

679	hydrothermal barite. A comparison of formation temperatures with modeled temperatures
680	based on fluid mixing indicate that conductive cooling lowers the temperatures within the
681	chimney walls by 60 to 120°C. Fluid salinity measurements provide the first direct evidence of
682	past venting of a fluid with a brine component from the Main Endeavour Field.
602	
683	logether, these results demonstrate the utility of barite for recording the chemical and physical
684	environment within the walls of an actively-forming hydrothermal vent. Petrogenetic
685	relationships between barite and other minerals can then be used to infer the conditions under
686	which other mineral phases, and microorganism colonies, grow within chimney walls.

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899 Figures
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Figure 1:



- 902 Figure 1: Bathymetric map of the Endeavour Segment, with the locations of the major active
- 903 vent fields. Inset map shows the location of the Endeavour Segment on the Juan de Fuca Ridge.
- Bathymetric data collected using hull-mounted EM300 multibeam system on the *R/V Thomas*
- 905 *G. Thompson* (TN146) (Kelley, 2002; <u>www.geomapapp.org</u>)

Figure 2:



906

907 Figure 2: A: Plane-polarized photomicrograph of ALV2467-R2, with a fluid conduit infilled by 908 tabular barite. The conduit is lined with dark-red to opaque rounded sphalerite grains. The 909 surrounding matrix consists of bladed barite, fine sphalerite with minor pyrite and late-stage 910 amorphous silica. B: Cross-polarized photomicrograph of ALV2464-R4, showing tabular and 911 bladed barite crystals that grew into open pore space. Yellow dashed boxes in A and B show 912 location of detailed images in C and D, respectively. C: Cross-polarized photomicrograph of 913 tabular barite crystal from A. The magenta colour within the blue crystal indicates Sr-rich 914 growth zones. D: Coloured electron microprobe backscatter image of barite crystal from B. 915 Again, magenta colours indicate Sr-rich growth zones.



Figure 3: Transmitted light photomicrographs (plane-polarized in left column, cross-polarized in
right column) showing the range of crystal morphologies for barite crystals within hydrothermal
vents from the Endeavour Segment. A: Euhedral tabular and bladed crystals; B: bladed crystals;

920 C: radiating acicular crystals; and D: acicular and dendritic crystals.





Figure 4: A: Plot of whole rock Ca vs. Ba for 335 chimney samples from all major vent fields andinactive vent sites within the axial valley showing a distinct negative correlation, with Ba-rich

samples having low Ca concentrations, and Ca-rich samples having low Ba concentrations.

925 Samples B: Strontium concentration plotted against Ba concentration. Samples are grouped as

- 926 either Ca-rich (red triangles) or Ca-poor (black circles). Because Sr partitions predominantly
- 927 into anhydrite or barite, the low concentrations of Ca in the Ba-rich samples indicates that
- 928 barite is the primary host for Sr in these samples, and whole rock Sr/Ba samples are
- 929 representative of the barite phase.

Figure 5:



- Figure 5: Electron microprobe backscatter images of barite crystals from samples ALV2467-R2
 (A and C) and ALV2464-R4 (B and D) showing Sr-rich (dark) and Sr-poor (light) growth zones.
 Numbers in A and B refer to the percent Sr occupying the cation site within barite, normalized
 to 100% Ba+Sr+Ca. Panels C and D show locations of laser ablation analyses. Lines A-H in C
 represent locations of elemental analyses summarized in Table 2. Lines 1-5 (C, outlined in
- 936 yellow) and the closely-spaced parallel lines 1-21 (D) are locations of ⁸⁷Sr/⁸⁶Sr analyses,
- 937 summarized in Table 4.

Figure 6:



938

Figure 6: Results of ⁸⁷Sr/⁸⁶Sr variability and Sr-concentrations within single barite crystals from
ALV2464-R4 (A) and ALV2467-R2 (B). The locations of the laser raster for each analysis are
outlined on the associated backscatter. For ALV2467-R2, the rasters not outlined in yellow arev
from elemental analyses indicated in Fig. 5C. The relationship between Sr concentration and
zonation within the crystals can be clearly seen, with darker regions having a higher Sr/Ba. The
width of each data point on the plots is equal to the width of each ablation line (25 μm).
Uncertainties for relative Sr concentrations are smaller than the symbols.

Figure 7:



Figure 7: Plot of ⁸⁷Sr/⁸⁶Sr versus the relative intensity of Sr (a proxy for Sr-concentration within
the crystal) for samples ALV2464-R4 and ALV2467-R2. For ALV2464-R4 (black circles), there is
very little variation in Sr-isotope composition with concentration within the crystal. Analyses 16
and 21 were ignored when plotting the regression line, as these samples were contaminated by
large fluid inclusions. For ALV2467-R2 (open diamonds), a slight negative correlation is present,
indicating a decreasing contribution of seawater (lower ⁸⁷Sr/⁸⁶Sr) with higher Sr/Ba in the

953 crystal.

Figure 8:



- 955 Figure 8: Occurrence of fluid inclusions in barite and amorphous silica. A) Tabular, zoned barite
- 956 crystal comprising several growth zones delineated by primary fluid and solid inclusions. B)
- 957 Primary fluid inclusions in barite with variable vapor/liquid ratios. C) Late secondary
- 958 ("immature") inclusions in barite. D) Primary Inclusions in amorphous silica.

Figure 9:



960 Figure 9: Histogram of pressure-corrected fluid inclusion formation temperatures for barite and

amorphous silica. The majority of primary inclusions from well-formed barite crystals indicate

962 formation temperatures of between 180 and 240°C. Secondary barite inclusions and inclusions

963 within amorphous silica formed at lower temperatures (120 to 170°C).



Figure 10:

Figure 10: Results of chemical modelling of fluid mixing. A: Changes in free and total Ba²⁺, Sr²⁺ 965 and SO₄²⁻ concentrations as a function of both temperature and degree of mixing. B: Variation 966 in the relative proportions of different $SO_4^{2^2}$ -bearing species at different mixing temperatures. 967 968 C: Degree of super- or under-saturation of barite, anhydrite and amorphous silica as a function of fluid mixing temperature. Mineral precipitation occurs at saturation indices greater than 969 zero. Samples are plotted based on mixing temperatures determined using barite ⁸⁷Sr/⁸⁶Sr 970 values. Higher degrees of supersaturation result in formation of dendritic, as opposed to well-971 972 formed, barite.

Figure 11:



974 Figure 11: Whole rock and single crystal Sr/Ba (A) and apparent partition coefficients (B) plotted

against mixing temperature, showing a general decrease in Sr substitution at higher formation

976 temperatures. Open diamonds represent Sr/Ba from different zones within a single euhedral

977 barite crystal (Fig. 6B) and indicate variable Sr substitution over small changes in temperature.

978 Dark (Sr-rich) zones. Whole rock temperature uncertainties are smaller than the symbol size,

979 plotted temperature uncertainties for ALV2467-R2 are 2σ .

981 Tables

982

983 Table 1: Fluid compositions used in mixing calculations

	Endeavour Vent Fluid ¹	Seawater ²
Temperature (°C)	350	2
pH (25°C)	4.2	8
Mg mmol/kg	0	53.2
Cl mmol/kg	425	550
Na mmol/kg	320	460
Ca mmol/kg	32.7	10.3
K mmol/kg	24.4	10.2
SiO2 mmol/kg	15.7	0.1
Fe mmol/kg	915	0
Mn mmol/kg	289	0
Ba mmol/kg	31	0.1
Sr mmol/kg	134	87
SO4 mmol/kg	0	28.3
H ₂ S mmol/kg	5.4	0
CO₂ mmol/kg	12.6	2.5
H₂ umol/kg	42	Log fO ₂ = -0.759
NH₃ umol/kg	500	4
⁸⁷ Sr/ ⁸⁶ Sr	0.7034 ³	0.7092 4

984 ¹ Endeavour vent fluid chemistry is from the Grotto vent (Butterfield et al., 1994) with Ba from 985 Seyfried et al. (2003), H_2 from Lilley et al. (1993), NH_3 of 500 as an approximate value.

986 ² Seawater values from Butterfield et al. (1994), Seyfried et al. (2003) and Tivey (2004).

- 987 ³ This study (see text)
- 988 ⁴ From Butterfield et al. (2001)

989

Table 2: Major element concentrations in barite from ALV2467-R2. Locations correspond to

991 laser ablation tracks in Figure 5C.

	Ba (ppm)	Sr (ppm)	Ca (ppm)	K (ppm)	S (ppm)	Total (%)
Line A	599290 ± 7	17431 ± 10	5079 ± 13	235 ± 15	133354 ± 9	103
Line B	569107 ± 7	21861 ± 7	8869 ± 5	348 ± 8	145591 ± 10	102
Line C	574770 ± 7	13567 ± 7	4299 ± 6	142 ± 9	130201 ± 9	100
Line D	571165 ± 7	22806 ± 8	8228 ± 6	287 ± 9	141458 ± 9	102
Line E	594443 ± 7	25697 ± 7	11357 ± 4	418 ± 8	145274 ± 10	105
Line F	582290 ± 7	14588 ± 8	4644 ± 7	157 ± 14	133655 ± 9	101
Line G	594681 ± 7	7557 ± 8	1971 ± 7	42 ± 21	136006 ± 9	101
Line H	626983 ± 7	11650 ± 10	3621 ± 11	104 ± 18	142375 ± 9	106

992 Table 3: Bulk ⁸⁷Sr/⁸⁶Sr, calculated fluid mixing and fluid mixture temperatures for hydrothermal chimneys samples.

	Barite crystal			% Hydrotherma	I Temperature of	[Sr]/[Ba]	[Sr]/[Ba]	Apparent
Sample	habit	Vent Field	⁸⁷ Sr/ ⁸⁶ Sr ± 2σ	fluid ¹	fluid mixture (°C) ²	(Whole Rock) ³	(Fluid) ⁴	K_{D^5}
ALV4450-1829	Acicular/bladed	Mothra	0.705461 ± 0.000009	49	173	0.045	2.52	0.007
ALV1452-1A	Dendritic	Main Endeavour	0.707581 ± 0.000011	17	61	0.069	2.62	0.004
ALV4446-1628	Acicular/bladed	Main Endeavour	0.706058 ± 0.000009	39	136	0.050	2.53	0.006
ALV3589-R2	Small tabular	Main Endeavour	0.705635 ± 0.000010	46	162	0.051	2.52	0.007
ALV2072-7	Acicular	Main Endeavour	0.705116 ± 0.000010	56	196	0.063	2.51	0.010
ALV2415-1D(3)	Acicular	Main Endeavour	0.704525 ± 0.000010	69	242	0.048	2.50	0.009
ALV1452-2	Acicular	Main Endeavour	0.704496 ± 0.000007	70	244	0.046	2.50	0.008
ALV2449-1	Acicular	Main Endeavour	0.704380 ± 0.000010	72	254	0.018	2.50	0.003
TiveyMisc2	Small tabular	Main Endeavour	0.704198 ± 0.000012	77	270	0.022	2.50	0.004
ALV2068-1	Acicular/bladed	Main Endeavour	0.704779 ± 0.000010	63	221	0.056	2.50	0.010
ALV2467-R2	Tabular	North of Main Endeavour	0.703798 ± 0.000009	88	308	0.020	2.49	0.004
ALV2467-R3	Acicular/bladed	Clam Bed	0.704816 ± 0.000011	62	218	0.008	2.50	0.001
ALV2467-R9	Tabular	North of Clam Bed	0.703862 ± 0.000011	86	301	0.026	2.49	0.005
ALV2461-R6-4	Acicular	High Rise	0.704630 ± 0.000010	66	233	0.025	2.50	0.004
ALV2464-R4	Tabular	High Rise	0.704584 ± 0.000009	67	237		2.50	
ALV3000C	Acicular	Salty Dawg	0.704545 ± 0.000009	68	240	0.021	2.50	0.004

993 1 % relative contribution calculated using equation (2).

994 ² Temperatures are calculated using equation (3).

³ Ratio determined using whole rock Sr and Ba concentrations (see Supplementary Table S1).

⁴ Calculated based on the degree of mixing (using ⁸⁷Sr/⁸⁶Sr) between endmember seawater and hydrothermal fluids (see Table 1 for

997 details).

998 ${}^{5} D_{Sr} = ([Sr]/[Ba])_{Whole Rock}/([Sr]/[Ba])_{Fluid}$

Table 4: Laser ablation strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) across single barite crystals from
samples ALV2464-R4 and ALV2467-R2.

Analysis ¹	⁸⁷ Sr/ ⁸⁶ Sr ± 2σ	Relative Sr intensity ² $\pm 2\sigma$	% Hydrothermal Fluid ³	Temperature ⁴ (°C)
ALV2464-R4				
1	0.70447 ± 0.00022	4.73 ± 0.14	70	246
2	0.70468 ± 0.00026	3.36 ± 0.11	65	229
3	0.70434 ± 0.00029	4.27 ± 0.15	73	257
4	0.70456 ± 0.00029	4.60 ± 0.16	68	239
5	0.70442 ± 0.00026	4.74 ± 0.12	71	250
6	0.70453 ± 0.00024	3.67 ± 0.02	69	241
7	0.70447 ± 0.00027	5.55 ± 0.05	70	246
8	0.70438 ± 0.00024	3.23 ± 0.03	72	253
9	0.70449 ± 0.00020	2.60 ± 0.01	70	245
10	0.70413 ± 0.00020	4.71 ± 0.02	79	275
11	0.70439 ± 0.00026	5.07 ± 0.04	72	253
12	0.70431 ± 0.00027	5.42 ± 0.06	74	260
13	0.70445 ± 0.00027	6.75 ± 0.04	71	248
14	0.70442 ± 0.00025	5.81 ± 0.05	71	250
15	0.70428 ± 0.00025	4.06 ± 0.03	75	263
16	0.70485 ± 0.00022	3.09 ± 0.04	62	216
17	0.70421 ± 0.00023	4.44 ± 0.04	77	268
18	0.70436 ± 0.00025	7.83 ± 0.03	73	255
19	0.70436 ± 0.00021	8.14 ± 0.12	73	256
20	0.70463 ± 0.00025	2.62 ± 0.12	66	233
21	0.70509 ± 0.00025	1.34 ± 0.04	56	198
ALV2467-R2				
1	0.70394 ± 0.00021	4.22 ± 0.05	84	294
2	0.70373 ± 0.00018	5.80 ± 0.04	90	314
3	0.70401 ± 0.00019	4.04 ± 0.01	82	287
4	0.70392 ± 0.00022	6.04 ± 0.01	84	295
5	0.70435 ± 0.00025	1.91 ± 0.03	73	257

1001 ¹Analysis numbers correspond to locations shown on Fig. 5D

1002 ² Relative Sr intensity, measured during laser ablation analysis can be used as a proxy for Sr-

1003 concentration within the barite crystal

1004 ³% hydrothermal fluid is calculated using equation (2)

1005 ⁴ Temperature is calculated using equation (3)

Inclusion #	Final Melting	Salinity
	Temperature (T _m , °C)	(wt. %) ¹
ALV2464-R4 (I	Barite)	
1	-5.1	8.0
2	-3.8	6.2
3	-5.1	8.0
4	-5.3	8.3
5	-5.4	8.4
6	-4.6	7.3
7	-5.6	8.7
8	-3.5	5.7
ALV2467-R2 (I	Barite)	
1	-3.5	5.7
2	-4.7	7.4
ALV2464-R4 (/	Amorph. Silica)	
1	-2.0	3.4

1007 Table 5: Calculated fluid salinities from fluid inclusions

1008 ¹ Calculated using equation 1

1009 Table 6: Partition coefficients for individual growth zones within a single barite crystal from ALV1010 2467-R2.

Analyzed	Sr/Ba	Sr/Ba	Apparent
Pair ¹	(fluid) ²	(barite) ³	K _D ⁴
2 - B	5.09	0.04	0.008
3 - C	5.09	0.02	0.005
4 - D	5.09	0.04	0.008
5 - F	5.21	0.03	0.005

1011 ¹ Number/letter combinations refer to paired analyses from single growth zones in Fig. 5C.

² Calculated using predicted fluid chemistry based on degree of mixing (determined by ⁸⁷Sr/⁸⁶Sr)
 and endmember fluid properties (Table 1).

1014 ³ Calculated using data in Table 2.

1015 4 K_D = ([Sr]/[Ba])_{Barite} /([Sr]/[Ba])_{Fluid}

1017 SUPPLEMENTARY INFORMATION

Table S1: Bulk geochemical analyses of sulfide samples from hydrothermal deposits along the
 Endeavour Segment.

Sample	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Analysis Detection Limit	INAA 0.005 wt %	ICP-ES	ICP-ES	
	0.005 Wt.%	0.01 wt.%	0.001 Wt.%	
ALV1417-1a b2	8.800	0.14	0.2000	0.023
ALV1417-10 02	0.029	0.11	0.0011	0.038
	1.200	0.16	0.0410	0.034
ALV1417-10 D2	8.900	0.10	0.2200	0.025
	0.470	0.07	0.0091	0.019
	0.003	0.04	0.0011 h.d	0.595
ALV1417-16 ALV1417-29 b5	2 100	0.00	0.0540	0.026
ALV1417-26	0.016	0.12	0.0040	0.020
ALV1417-50	0.010	0.00	b d	0.000
ALV1417-56 b12	0.002	0.20	b.d. b.d	
ALV1417-5c b13	0.003	0.29	0 0024	0.800
ALV1417-5d b14	0.008	0.25	0.0024	0.300
AI V1417-c b9	0.011	0.07	b.d.	0.500
AI V1418-1d b2	0.007	0.06	b.d.	
AI V1418-1d b5	1.400	0.04	0.0210	0.015
Al V1418-1e b2	37.00	0.31	0.6900	0.019
AI V1418-3a	1.400	0.04	0.0210	0.015
ALV1418-6b b9	1.300	0.12		
ALV1418-8b b6	0.012	0.06	0.0001	0.008
ALV1419-1a b2	1.300	0.13	0.0470	0.036
ALV1419-1b b3	0.021	0.03	0.0011	0.052
ALV1419-1c b2	37.00	0.32	0.6900	0.019
ALV1419-1d b3	39.00	0.29	0.7400	0.019
ALV1419-1d b31	22.00	0.23	0.4300	0.020
ALV1419-1h b4	32.000	0.31	0.6900	0.022
ALV1419-2 b10	0.008	0.01	b.d.	
ALV1439	0.300	0.33	0.0193	0.064
ALV1445-3A		1.52	b.d.	
ALV1445-3B		8.36	b.d.	
ALV1445-3C		6.80	b.d.	
ALV1445-3D		3.35	b.d.	
ALV1445-7	0.250	0.03	0.0139	0.056
ALV1447-1		10.30	0.0881	
ALV1451-1	0.290	0.33	0.0205	0.071
ALV1452-1A	12.00	0.25	0.8230	0.069
ALV1452-2	8.500	0.16	0.3880	0.046
ALV2057	0.340	0.03	0.0155	0.046
ALV2061-2A	0.022	5.83	0.0399	1.814
ALV2061-2B	0.034	1.04	0.0074	0.218
ALV2063-1B	0.094	0.41	0.0085	0.090
ALV2066-3	0.016	17.20	0.1140	7.125
ALV2066-4A	0.520	0.28	0.0251	0.048
ALV2066-4B	0.003	0.23	0.0015	0.600
ALV2066-5	0.003	34.10	0.0856	34.240
ALV2060-6	0.003	0.16	0.0022	0.880
ALV2000-1	23.00	0.34	1.2800	0.056
ALV2072-78	7.500	0.19	0.6440	0.086
ALV2012-1 ALV2072 1	5.000	0.15	0.3170	0.003
ALV2013-1	0.110	25.80	0.1970	1.791
		27.10	1 2200	
		0.27	1 1100	
ΛΕνζΙΙΟ-Ν4α-4 ΔΙ \/2404 4	0.002	4.41	1.1100	2 220
ΔΙ \/2404-1	0.003	1.00	0.0083	0.200
AL V2404-3R	0.003	0.02	0.0005	0.046
, L V 2 T U T U D	0.200	0.07	0.0130	0.040

Sample Analysis	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Detection Limit	0.005 wt.%	0.01 wt.%	0.001 wt.%	
AI \/2404-4	0.890	0.03	0.0357	0 040
ALV2406-1A	0.120	0.18	0.0107	0.040
ALV2406-1B	0.003	8.71	0.0375	15.000
ALV2408-1A	1.650	0.11	0.0813	0.049
ALV2408-1B	0.003	1.62	0.0125	5.000
ALV2409-1B	0.082	0.04	0.0019	0.023
ALV2411-1A	0.035	30.70	0.2950	8.429
ALV2411-2	0.003	0.11	0.0005	0.200
ALV2412-1	0.220	0.03		
ALV2413-2	0.003	0.09	0.0005	0.200
ALV2414-1	0.078	5.91	0.0462	0.592
ALV2415-1D(1)	0.870	0.08	0.0443	0.051
ALV2415-1D(2)	0.003	0.10	0.0005	0.200
ALV2415-1D(3)	2.700	0.10	0.1300	0.048
ALV2418-1	0.010	0.01	0.0005	0.050
ALV2419-1	0.023	0.04	0.0005	0.022
ALV2419-2	0.023	10.80	0.0795	3.457
ALV2420-1B	0.061	1.18	0.0105	0.172
	0.370	0.27	0.0241	0.005
ALV2420D ALV2448-1	0.013	27.70	0.1820	12.155
ΔΙ \/2440-1	0.003	4.94	0.0332	0.018
AL V2450-2	0.240	0.05	0.0065	0.027
ALV2450-3b (crust)	0.2.10	0.06	0.0370	0.027
ALV2451-1	0.028	1.46	0.0092	0.329
ALV2452-1	0.015	1.15	0.0097	0.647
ALV2452-2	1.650	0.03	0.0373	0.023
ALV2453-1A	0.044	0.07	0.0015	0.034
ALV2453-1B	0.015	1.11	0.0081	0.540
ALV2453-2 (puffer)	0.003	0.51	0.0032	1.280
ALV2453-3	0.010	0.06	0.0010	0.100
ALV2460 B	0.440		0.0010	0.002
ALV2460 E	0.080		0.0010	0.013
ALV2460-R2-14a	2.600	0.06	0.0440	0.017
ALV2460-R2-14b	0.580	0.04	0.0065	0.011
ALV2460-R2-15	0.860	0.07	0.0250	0.029
ALV2400-R3-3	1.200	0.10	0.0400	0.033
ALV2400-R3-5	0.380	6.45	0.0330	0.030
$A = \sqrt{2400 - 13 - 3}$	0.730	0.45	0.0730	0.057
AL V2460-R5	0.041	26.27	0.2100	5.122
AL V2460-R5P1C	0.0.12	31.90	0.2440	0.122
ALV2460-R5P2C		38.70	0.2700	
ALV2460-R5P3B-D		35.70	0.2790	
ALV2461 A	8.870		0.2800	0.032
ALV2461 E	0.630		0.0215	0.034
ALV2461-R10-2		0.08	0.0017	
ALV2461-R10b2	0.015	0.06	0.0010	0.067
ALV2461-R11-9	1.200	1.19	0.0380	0.032
ALV2461-R12-2	0.280	1.78	0.0200	0.071
ALV2461-R13 TIP	4.600	0.21	0.1000	0.022
ALV2461-R13/1	0.280	0.06	0.0120	0.043
ALV2461-R13/2	0.320	0.04	0.0110	0.034
ALV2461-R13/3	1.100	0.07	0.0280	0.025
ALV2461-R13/4	5.600	0.20	0.0950	0.017
ALV2461-R13-4-BOT	0.970	0.06	0.0350	0.036
ALV2401-K102	0.730	0.07	0.0290	0.040
ALV2401-K-3		0.07	0.0334	
ALV2401-R-J-2	0.009	0.01	0.0005	2 000
AL V2461-R4-2	0.008	0.04	0.0100	2.000
Al V2461-R4d	0.007	0.03	0.0003	0.143
ALV2461-R6-4	1.500	0.22	0.0370	0.025
		0.22		

Sample	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Analysis Detection Limit	0 005 w/t %	1CF-ES	1CF-ES 0 001 w/+ %	
	0.003 WL.%	0.01 WL.70	0.001 WL.%	0.020
ALV2401-K/C2	1.700	0.10	0.0440	0.026
ALV2401-RÖ-J	0.025	22.92	0.2200	8.800
ALV2462 A1	4.070	0.44	0.1480	0.030
ALV2462-R1a	0.760	0.44	0.0240	0.032
ALV2462-R10	0.041	26.49	0.2500	6.098
ALV2462-R1C	0.620	0.13	0.0210	0.034
ALV2462-R6-1d2	0.070	0.09	0.0028	0.040
ALV2462-R7-1b	0.600	4.26	0.0420	0.070
ALV2463 A	0.010		0.0010	0.100
ALV2463 F	0.003		0.0010	0.400
ALV2463-R1-2	0.010	0.10	0.0010	0.100
ALV2463-R2-1a	0.007	0.09	0.0010	0.143
ALV2463-R2-3		0.02	0.0005	
ALV2463-R2P2B			0.0005	
ALV2463-R3-3	22.00	0.20	0.3650	0.017
ALV2463-R3-misc			b.d.	
ALV2463-R4-pc	26.00	0.22	0.5700	0.022
ALV2463-R5c2		0.04	0.0715	_
ALV2463-R5c3	1.800	0.09	0.0290	0.016
ALV2463-R6-misc	0.003	0.04	0.0010	0.400
ALV2463-R7-6B	0.220	0.01	b.d.	
ALV2463-R7-6C	10.70	0.45	0.3610	0.034
ALV2463-R7-6G	30.50	0.01	0.8900	0.029
ALV2464 B	0.003		0.0010	0.400
ALV2464 F-V	0.010		0.0010	0.100
ALV2464-R4		0.11	0.1290	
ALV2464-R5-3	1.700	0.08	0.0380	0.022
ALV2464-R6-2c	0.620	0.19	0.0250	0.040
ALV2464-R6P1C		0.10	0.1200	
ALV2464-R6-pc		0.09	0.0683	
ALV2464-R8-1b	1.100	0.13	0.0370	0.034
ALV2465-R1-6c	0.760	0.12	0.0210	0.028
ALV2465-R1P1A		14.80	0.1270	
ALV2465-R2-1e	0.008	5.50	0.0460	5.750
ALV2465-R2-2a2	0.035	18.56	0.1600	4.571
ALV2465-R2-2d2	0.094	25.49	0.2000	2.128
ALV2465-R2-3b	0.060	11.85	0.1100	1.833
ALV2465-R2A	0.003	8.93	0.0700	28.000
ALV2465-R2b	0.039	1.48	0.0100	0.256
ALV2465-R3-2a	0.029	21.35	0.2000	6.897
ALV2466 A	0.890	0.06	0.0311	0.035
ALV2466 E	1.130	0.04	0.0282	0.025
ALV2466-b	0.170	2.46	0.0220	0.129
ALV2466-c	0.200	0.06	0.0080	0.040
AI V2466-R1	0.200	0.02	0.0005	5.010
AI V2466-R1-4h	0.007	0.09	0.0028	0.400
AI V2466-R1P3R2	5.007	0.05	0.0005	0.100
AI \/2466-R3	0 2 2 0	0.01	0.0003	0 025
AI \/2466-R3-1h1	0.330	0.04	0.0001	0.023
AI \/2466-R3-162	0.430	0.07	0.0120	0.027
ΔI \/2466-R4	0.570	0.00	0.0113	2 121
$\Delta = \sqrt{2400} + 14$	0.019	5.71	b d	5.421
ALV2400-R4-11180	0.420	0 1 2	0.0100	0.044
ALV2400-RJ-0/1	0.430	0.12	0.0190	0.044
ALV2400-RJ-0/2	0.015	1.78	0.0120	0.800
MLV2400-RJ-0/J	0.020	0.06	0.0010	0.050
ALV2400-R3-0/4	0.610	0.09	0.0190	0.031
	0.000	10.60	0.2190	0 222
ALV2407-K1-140	0.069	2.46	0.0230	0.333
ALV240/-R1-103	0.054	0.65	0.0065	0.120
ALV2467-R16XC	0.040	20.85	0.1900	4.750
ALV2467-R2	23.10	0.07	0.4560	0.020
ALV2467-R3	26.50	0.15	0.2000	0.008
ALV2467-R4-misc	0.013	0.04	0.0010	0.077

Sample	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Andlysis Detection Limit	11NAA 0.005 w/+ %	ICP-ES 0.01 w/t %	ICP-ES 0 001 w/+ %	
	0.003 WL.%	0.01 WL.%	0.001 WL.%	0.020
ALV2401-KY ALV2927-A	8.650	0.01	0.2240	0.026
ALV2927-A	2.700	0.10	0.1190	0.044
ημν <i>ζήζι-</i> Φ ΔΙ \/2020	0.024	20.07	0.0005	6 765
ALV2929 ALV2936-A	0.034	29.00	0.2300	0.703
ΔI V/2936-R	1 150	0.05	0.0140	0.050
ALV2996MEE	0.003	0.00	0.0005	0.200
AI V2997AH	0.041	27.00	0.2090	5.098
ALV2998-A	0.003	0.04	0.0005	0.200
ALV2998-B	0.550	0.39	0.0133	0.024
ALV2998-Salut (1of2)	0.150	6.09	0.0557	0.371
ALV2998-Salut (2of2)	0.220	6.44	0.0630	0.286
ALV3000C	1.700	0.08	0.0365	0.021
ALV3000-GrendleA	0.180	0.04	0.0098	0.054
ALV3000-SpireB	2.200	0.11	0.0443	0.020
ALV3003	0.870	0.42	0.0204	0.023
ALV3005A	0.320	11.70	0.0921	0.288
ALV3005B	0.036	0.02	0.0023	0.064
ALV3569-R1-A	0.026	11.20	0.0688	2.646
	0.560	0.21	0.0156	0.028
		10.80	0.0872	
ALV3370-111136(B)	0.490	2.10	0.0147	0 067
ALV3010-RZ	0.480	2.99	0.0321	1 250
ALV3370-R2D ALV3572-R1	0.120	20.00	0.1020	1.350
ALV3572-R1 ALV3581-R-1	33.00	0.03	0.0027	0.018
AL V3581-R-2	0.073	22.60	0.1860	2.548
ALV3586-R-1A	0.003	0.23	0.0022	0.880
ALV3586-R-1B	0.017	0.32	0.0029	0.171
ALV3587-R-1	6.100	0.07	0.1150	0.019
ALV3587-R-2	0.026	29.10	0.2580	9.923
ALV3588-A	0.200	10.30	0.0804	0.402
ALV3588-B (R1)	0.029	32.40	0.2780	9.586
ALV3588-R2A	0.580	6.28	0.0957	0.165
ALV3588-R2B	0.930	0.03	0.0337	0.036
ALV3589-R2	11.00	0.17	0.5570	0.051
ALV3609-01A	0.003	23.20	0.1490	59.600
ALV3612-01	0.022	26.00	0.2040	9.273
ALV3616-03	0.130	0.02	0.0056	0.043
ALV3616-A	0.790	0.05	0.0256	0.032
4LV3010-B	4.100	0.09	0.0975	0.024
HLV3019-01	0.003	0.64	0.0046 b.d	1.840
¬∟νου∠∠ ΔΙ\/3622_01Λ	0.003 5.400	0.01	0.00 0.1000	0 027
1 1/3622-01A	0.040	0.21	0.1990	0.037
	0.040	0.01	0.0027	0.008
ALV3623-02	0.003	0.01	0.0011	0.440
AI V4438-1635	0.013	0.01	0.0005	0.035
ALV4438-1816	0.308	4.88	0.0566	0.184
ALV4438-1816 (inner)	0.350	0.10	0.0289	0.083
ALV4438-1816 (outer)	0.625	0.01	0.0440	0.070
ALV4438-2132	0.003	0.01	0.0025	1.000
ALV4441-1912	0.500	0.01	0.0336	0.067
ALV4441-2135	0.019	3.46	0.0188	0.989
ALV4446-1628	1.250	0.07	0.0631	0.050
ALV4446-1735	1.190	15.67	0.1580	0.133
ALV4448-2211	0.863	0.01	0.0429	0.050
ALV4449-1630	2.130	0.24	0.1510	0.071
ALV4449-1938	0.025	37.21	0.1970	7.880
ALV4449-1938 (inner)	0.054	39.45	0.1870	3.463
ALV4449-1938 (outer)	0.033	7.82	0.0424	1.285
ALV4450-1538	0.077	38.89	0.2210	2.870
ALV4450-1538 (inner)	0.040	24.90	0.1260	3.150

Sample	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Analysis Detection Limit	INAA 0.005 wt %	ICP-ES	ICP-ES	
	0.003 WL.%	0.01 WL.%	0.001 WL.%	0.045
ALV4450-1829	22.10	0.39	1.0000	1.095
ALV4451-1725 ALV/4452-1706	0.208	38.05 10.23	0.2260	1.08/
ΔΙ \/4517-1703	0.377	0.01	0.0730	0.211
AL V4517-1718	0.702	0.01	0.0574	0.082
AI V4518-1836	0.025	38.05	0.2370	9.480
ALV4518-1836 (inner)	0.020	29.10	0.1690	8.450
ALV4518-1836 (outer)	0.013	36.09	0.2270	17.462
ALV4525-0134	0.713	0.06	0.0598	0.084
ALV-Grotto-Sep95	0.003	0.01	0.0005	0.200
D264-R2	0.003	0.01	0.0006	0.240
D264-R22	6.120	0.17	0.3630	0.059
D264-R3	0.666	0.07	0.0423	0.064
D264-R5	2.610	0.18	0.1950	0.075
D264-R6	0.035	0.01	0.0048	0.137
D265-R2	0.003	0.04	0.0011	0.440
D265-R3	0.003	0.04	0.0004	0.160
D265-R4	0.003	0.10	0.0011	0.440
D265-R8	2.250	0.18	0.1190	0.053
D266-R4	9.900	0.11	0.2330	0.024
	0.477	0.13	0.0250	0.054
	0.003	0.07	0.0074	2.900
D200-N8	2 520	0.07	0.0013	0.000
Endu-1 vent	0.007	0.55	b d	0.056
FINN-CPY	0.750	0.07	0.0293	0.039
FINN-SPH	4.900	2.00	b.d.	0.005
FINN-ZN Silica		1.69	0.1910	
G2 mucus	0.003	1.00	0.0050	2.000
HYS 270-1	0.003	0.04	0.0005	0.200
HYS 278-14	0.003	0.02	0.0005	0.200
HYS 278-3	0.011	0.26	0.0021	0.191
HYS 278-4	1.300	0.04	0.0438	0.034
HYS 278-9	0.003	0.01	0.0005	0.200
HYS 280-16	1.100	0.01	0.0537	0.049
HYS-278-01	0.980	0.04	0.0227	0.023
HYS-278-02a	1.200	0.06	0.0350	0.029
HYS-278-02b	0.850	0.04	0.0406	0.048
HYS-278-09a	0.003	0.01	0.0006	0.240
HYS-278-090	0.003	0.01	0.0003	0.120
HYS-278-10	0.057	0.01	0.0016	0.028
UVS 278 1/2	0.003	0.01	0.0003	0.200
HVS-270-14a	0.003	0.01	0.0002	0.080
HVS-278-16	2 800	0.01	0.0002	0.000
HYS-347-01	1 800	0.04	0.0258	0.002
HYS-347-02	0.010	1.07	0.0105	1.050
HYS-350-01	0.240	1.13	0.0162	0.068
HYS-350-02	0.017	1.63	0.0161	0.947
HYS-350-02(a)	25.00	0.27	0.0990	0.004
HYS-355-01	0.047	0.11	0.0006	0.013
HYS-355-02	0.003	0.03	0.0002	0.080
HYS-355-B	4.800	5.83	0.0761	0.016
HYS-356-01A	0.048	2.73	0.0226	0.471
HYS-356-01B	0.003	1.06	0.0074	2.960
HYS-356-02A	0.045	16.60	0.1648	3.662
HYS-363-01A	0.015	1.47	0.0141	0.940
HYS-363-01B	11.00	0.40	0.0226	0.002
HYS-363-01C	0.007	0.33	0.0033	0.508
J2-52-1	0.039	5.84	0.0412	1.056
J2-59-1	0.044	37.20	0.2730	6.205
J2-59-2	0.110	3.76	0.0336	0.305
J2-59-4 Misc	0.990	0.05	0.0561	0.057

Sample	Ba (wt. %)	CaO (wt. %)	Sr (wt. %)	Sr/Ba
Analysis	INAA	ICP-FS	ICP-ES	0.720
Detection Limit	0.005 wt.%	0.01 wt.%	0.001 wt.%	
J2-59-4D	0.003	0.04	0.0005	0.200
Pisces 1B	0.003	0.43	0.0149	5.960
R1348-1007-Ba	0.000	0.03	0.0129	180.926
R1348-1007-S	0.002	0.08	0.0009	0.390
R507-9	0.047	37.80	0.2490	5.298
TIVEY MISC-1	0.875	0.09	0.0971	0.111
TIVEY MISC-2	33.00	0.15	0.7160	0.022
TIVEY MISC-3	0.008	0.03	0.0005	0.063
TIVEY MISC-4	0.580	0.07	0.0496	0.086
TIVEY MISC-5	0.170	7.22	0.0657	0.386
TIVEY MISC-6	0.100	0.01	0.0035	0.035
TIVEY MISC-7	1.100	0.02	0.0444	0.040
TT 170-66D 1B	0.380	0.07	0.0140	0.037
TT 170-66D AIS 9T 1	0.030	0.01	0.0011	0.037
TT 170-66D AIS 9T 2	0.003	0.01	0.0010	0.400
TT 170-66D AIS Inner 1	0.048	0.02	0.0019	0.040
TT 170-66D AIS Inner 2	0.042	0.01	0.0016	0.038
TT 170-66D AIS Slab 1	0.049	0.01	0.0018	0.037
TT 170-66D AIS Slab 2	0.051	0.01	0.0016	0.031
TT 170-66D B112A	0.025	0.01	0.0005	0.020
TT 170-66D B19-B2	0.021	0.01	0.0015	0.071
TT 170-66D B1-B2	0.003	0.01	0.0005	0.200
TT 170-66D B30-A	0.060	0.01	0.0027	0.045
TT 170-66D B9-B	0.003	0.03	0.0013	0.520
TT 170-66D EXIT CH 1	0.026	0.02	0.0005	0.019
TT 170-66D EXIT CH 2	b.d.	0.13	0.0005	
TT 170-66D R2	0.003	0.01	0.0005	0.200

b.d.: Below detection limits

1022 Table S2: Relative cation concentrations in barite from electron microprobe analysis1023 (normalized to total Ba+Sr+Ca)

Sample	Analysis	Ba (%)	Sr (%)	Ca (%)
ALV2072-7	1	86.7	6.7	6.7
	2	86.7	6.7	6.7
	3	84.4	8.9	6.7
	4	84.4	8.9	6.7
	5	88.9	6.7	4.4
	6	86.7	6.7	6.7
	7	84.4	6.7	6.7
ALV3589-R2	1	95.5	4.6	b.d.
	2	97.7	2.3	b.d.
	3	100.0	b.d.	b.d.
	4	95.5	4.6	b.d.
	5	93.0	7.0	b.d.
	6	95.4	4.7	b.d.
	7	97.7	2.3	b.d.
ALV2467-R2	1	95.5	4.6	n.d.
	2	90.9	9.1	n.d.
	3	97.7	2.3	n.d.
	4	95.4	4.7	n.d.
	5	97.7	2.3	n.d.
	6	93.2	6.8	n.d.
ALV2068-1	1	97.7	2.3	b.d.
	2	78.3	10.9	10.9
	3	80.0	17.8	2.2
	4	88.6	9.1	2.3
ALV2467-R3	1	95.5	4.6	b.d.
	2	93.0	7.0	b.d.
	3	97.7	2.3	b.d.
	4	97.7	2.3	b.d.
Tivey Misc-2	1	97.7	2.3	b.d.
	2	95.5	4.6	b.d.
	3	95.5	4.6	b.d.
	4	97.6	2.4	b.d.
	5	97.7	2.3	b.d.
	6	97.7	2.3	b.d.
ALV2464-R4	1	90.9	6.8	2.3
	2	97.7	2.3	b.d
	3	82.2	13.3	4.4
	4	95.5	4.6	b.d.
	5	88.6	11.4	b.d.
	6	100.0	b.d.	b.d.
	7	95.4	4.7	b.d.

b.d. = below detection limits, n.d. = not determined

1025

- 1026 Figure S1: Electron microprobe backscatter images showing locations of analyses reported in
- 1027 table S1.

- <image><image>
- 1029

1030



1031

1032 ALV2467-R2:



ALV2068-1:



- 1034 Figure S1 (cont.):
- 1035 ALV2467-R3:



1037 ALV 2464-R4:



1038 1039 Tivey Misc-2:



1040 Table S3: Laser ablation ICP-MS trace element results for ALV2467-R2. Analytical lines

1041 correspond to locations in Figure 5C.

	Li(7)	Be(9)	B(11)	Na(23)	Mg(24)	Al(27)	P(31)	S(33)	S(34)	К(39)	Ca(43)	Ca(44)	Sc(45)	Ti(49)	V(51)	Cr(52)	Cr(53)
	Li µg/g	ве µg/g	в µg/g	Na µg/g	Mg µg/g	AI µg/g	P µg/g	S µg/g	S µg/g	к µg/g	Ca µg/g	Ca µg/g	Sc µg/g	Πµg/g	v µg/g	Cr µg/g	Cr µg/g
barite line A (32µm, 2J/cm ⁻ , 10Hz)	n.a.	b.a.i.	1.8	9.8 76	b.a.i.	n.a.	55.4 20	126668	133354	234.6	5397.0 17	5079.3	b.d.I.	n.a.	n.a.	n.a.	n.a.
barite line B (32um 21/cm ² 10Hz)	nd	h d l	55	19.3	1.6	nd	32.1	140552	145591	348 3	9269.2	8868.8	h d l	29	hdi	nd	hdi
2RSD %			67	48	57		43	140552	10	8	9	5		74			
barite line C (32µm, 2J/cm ² , 10Hz)	b.d.l.	n.d.	n.d.	n.d.	b.d.l.	n.d.	32.8	128725	130201	142.4	4361.6	4298.8	n.d.	n.d.	b.d.l.	n.d.	n.d.
2RSD % barite line D (32µm, 2J/cm ² , 10Hz)	n.d.	b.d.l.	n.d.	13.9	n.d.	b.d.l.	41 45.6	9 134767	9 141458	9 286.9	15 7947.6	6 8228.1	n.d.	n.d.	ь.d.l.	ь.d.l.	 b.d.l.
2RSD %				82			34	9	9	9	9	6					
barite line E (32µm, 2J/cm², 10Hz) 2RSD %	b.d.l.	b.d.l.	b.d.l.	n.d.	b.d.l.	n.d.	41.6 30	138672 9	145274 10	418.3 8	11842.3 8	11357.3 4	n.d.	2.6 91	b.d.l.	b.d.l.	n.d.
barite line F (32µm, 2J/cm ² , 10Hz) 2RSD %	b.d.l.	n.d.	n.d.	17.5 82	b.d.l.	b.d.l.	31.2 44	131443 9	133655 9	156.8 14	4556.1 19	4644.0 7	0.4 94	n.d.	b.d.l.	b.d.l.	n.d.
barite line G (32µm, 2J/cm ² , 10Hz)	b.d.l.	n.d.	n.d.	8.2	b.d.l.	1.6	38.6	121514	136006	42.3	2175.3	1970.8	b.d.l.	2.0	n.d.	n.d.	n.d.
barite line H (32um, 21/cm ² , 10Hz)	ь.d.l.	b.d.l.	b.d.l.	97 n.d.	n.d.	95 b.d.l.	34.7	129821	9 142375	103.7	3963.8	, 3620.9	 b.d.l.	2.7	n.d.	n.d.	 n.d.
2RSD %							41	10	9	18	13	11		96			
Standards	liuø/ø	Re ug/g	B ug/g	Na ug/g	Mø 11ø/ø	Al 110/0	Ριισ/σ	Sug/g	Sug/g	K 119/9	Ca ug/g	Ca ug/g	Sc ug/g	Τί μα/σ	V 11 <i>9/9</i>	Cr 110/0	Cr 110/0
NIST612	40	38	34	101635	68	10744	47	377	377	62	85049	85049	40	44	39	36	36
NIST610_611	468	476	350	99409	465	10320	413	575	575	464	81476	81476	455	452	450	408	408
PGE_Ni7b	-	-	-	-	-	-	-	392000	392000	-	-	-	-	-	-	-	-
	Mp(EE)	Eo/E6)	Eo(57)	Co(50)	Ni(62)	Cu(62)	70(64)	62(71)	60(72)	Go(74)	Ac(75)	So(77)		Sr(99)	7r(00)	Nb(02)	Mo(QE)
	Mn ug/g	Fe ug/g	Fe ug/g		Ni ug/g		2n(04) 7n ug/g	Ga ug/g	Ge ua/a	Ge ua/a		Se ug/g	Rh ug/g	Sr 119/9	7r 119/9	Nh ug/g	Mo ug/g
barite line A (32um 21/cm ² 10Hz)	n.d.	22	h.d.l.	n.d.	h.d.l.	n.d.	8.6	n.d.	n d	h d l	h.d.l.	h.d.l.	n.d.	17431.2	h.d.l.	h.d.l.	n.d.
2RSD %		94					55							10			
barite line B (32µm, 2J/cm², 10Hz)	b.d.l.	n.d.	b.d.l.	b.d.l.	b.d.l.	n.d.	37.9	n.d.	n.d.	b.d.l.	n.d.	b.d.l.	n.d.	21860.6	b.d.l.	b.d.l.	b.d.l.
2RSD %	 h d l	 h d l	 n d	 n d	 n d	 n d	52	 n d	 n d	 n d	 n d	 n d		7	 n d	 n d	 n d
2RSD %							65						88	7			
barite line D (32µm, 2J/cm ² , 10Hz) 2RSD %	b.d.l.	n.d.	n.d.	n.d.	n.d.	1 81	8.1 84	n.d.	b.d.l. 	n.d. 	n.d.	n.d.	n.d.	22805.8 8	b.d.l.	b.d.l.	b.d.l.
barite line E (32µm, 2J/cm ² , 10Hz)	n.d.	n.d.	n.d.	n.d.	b.d.l.	n.d.	15 40	0.5	n.d.	b.d.l.	1.8	b.d.l.	b.d.l.	25697.2	b.d.l.	b.d.l.	b.d.l.
barite line F (32μm, 2J/cm ² , 10Hz)	n.d.	n.d.	b.d.l.	b.d.l.	b.d.l.	n.d.	40 7	n.d.	n.d.	1.0	b.d.l.	b.d.l.	n.d.	, 14588.5	n.d.	b.d.l.	b.d.l.
2RSD % barite line G (32um, 2J/cm ² , 10Hz)	0.4	 b.d.l.	 b.d.l.	 b.d.l.	 n.d.	 b.d.l.	50 n.d.	 n.d.	 b.d.l.	97 n.d.	 b.d.l.	 n.d.	 b.d.l.	8 7557.5	 b.d.l.	 b.d.l.	 n.d.
2RSD %	89													8			
barite line H (32µm, 2J/cm², 10Hz)	n.d.	18	b.d.l.	b.d.l.	n.d.	b.d.l.	12	0.4	5.2	n.d.	n.d.	b.d.l.	n.d.	11649.9	b.d.l.	n.d.	b.d.l.
2RSD %		84					51	73	64					10			
Standards	Mn μg/g	Fe µg/g	Fe µg/g	Co µg/g	Ni µg/g	Cu µg/g	Zn μg/g	Ga µg/g	Ge µg/g	Ge µg/g	As µg/g	Se µg/g	Rb µg/g	Sr µg/g	Zr µg/g	Nb µg/g	Mo µg/g
NIST612	39	51	51	36	39	38	39	37	36	36	36	16	31	78	38	39	37
NIST610_611	444	458	458	410	459	441	460	433	447	447	325	138	426	516	448	465	417
PGE_NI7D	-	568000	568000	-	47900	-	-	-	-	-	-	-	-	-	-	-	-
	Ru(101)	Rh(103)	Pd(105)	Ag(107)	Cd(111)	In(115)	Sn(118)					- (D (407)	C (4 47)	0 ((457)	TI (450)	Dv(163)
	Bu ug/g		• •		(,	(110)	311(110)	Sb(121)	Te(125)	Te(128)	Cs(133)	Ba(135)	Ba(137)	Sm(147)	Ga(157)	10(159)	0,(100)
barito lino A (22).m 21/am2 1011-1	κu μg/g	Rh µg/g	Pd µg/g	Ag µg/g	Cd µg/g	In µg/g	Sn µg/g	Sb(121) Sb µg/g	Te(125) Te μg/g	Te(128) Te µg/g	Cs(133) Cs µg/g	Ba(135) Ba μg/g	Ba(137) Ba μg/g	Sm(147) Sm μg/g	Gd(157) Gd µg/g	Tb(159) Tb μg/g	Dy µg/g
same me A (52µm, 2)/cm-, 10HZ)	b.d.l.	Rh μg/g b.d.l.	Pd µg/g n.d.	Ag μg/g n.d.	Cd µg/g b.d.l.	In μg/g n.d.	Sn μg/g b.d.l.	Sb(121) Sb μg/g b.d.l.	Te(125) Te μg/g b.d.l.	Te(128) Te μg/g n.d.	Cs(133) Cs µg/g 0.3	Ba(135) Ba μg/g 599113	Ba(137) Ba μg/g 599290	Sm(147) Sm μg/g n.d.	Gd(157) Gd μg/g n.d.	Tb(159) Tb μg/g n.d.	Dy μg/g b.d.l.
2RSD %	b.d.l.	Rh μg/g b.d.l. 	Pd μg/g n.d.	Ag μg/g n.d.	Cd μg/g b.d.l.	in μg/g n.d.	5n μg/g b.d.l.	Sb(121) Sb μg/g b.d.l.	Te(125) Te µg/g b.d.l.	Te(128) Te μg/g n.d.	Cs(133) Cs μg/g 0.3 52	Ba(135) Ba μg/g 599113 8	Ba(137) Ba μg/g 599290 7	Sm(147) Sm μg/g n.d.	Gd(157) Gd μg/g n.d.	Tb μg/g n.d.	Dy μg/g b.d.l.
2RSD % barite line B (32µm, 2J/cm ² , 10Hz) 2RSD %	b.d.l. 0.5 99	Rh μg/g b.d.l. n.d.	Pd μg/g n.d. n.d.	Ag μg/g n.d. b.d.l.	Cd μg/g b.d.l. n.d.	n.d. b.d.l.	5n μg/g b.d.l. b.d.l.	Sb(121) Sb μg/g b.d.l. n.d.	Te(125) Te μg/g b.d.l. n.d.	Te(128) Te μg/g n.d. n.d.	Cs(133) Cs μg/g 0.3 52 0.3 53	Ba(135) Ba μg/g 599113 8 585229 8	Ba(137) Ba μg/g 599290 7 569107 7	Sm(147) Sm μg/g n.d. n.d.	Gd(157) Gd μg/g n.d. b.d.l.	1b(159) Tb μg/g n.d. n.d.	Dy μg/g b.d.l. n.d.
2RSD % barite line B (32µm, 2J/cm ² , 10Hz) 2RSD % barite line C (32µm, 2J/cm ² , 10Hz)	b.d.l. 0.5 99 b.d.l.	Rh μg/g b.d.l. n.d. b.d.l.	Pd μg/g n.d. n.d. n.d.	Ag μg/g n.d. b.d.l. n.d.	Cd μg/g b.d.l. n.d. n.d.	n.d. n.d. b.d.l. b.d.l.	5n µg/g b.d.l. b.d.l. n.d.	Sb(121) Sb μg/g b.d.l. n.d. b.d.l.	Te(125) Te μg/g b.d.l. n.d. n.d.	Te(128) Te µg/g n.d. n.d. n.d.	Cs(133) Cs μg/g 0.3 52 0.3 53 0.2	Ba(135) Ba μg/g 599113 8 585229 8 597056	Ba(137) Ba μg/g 599290 7 569107 7 574770	Sm(147) Sm μg/g n.d. n.d. n.d.	Gd(157) Gd μg/g n.d. b.d.l. b.d.l.	Tb μg/g n.d. n.d. b.d.l.	Dy μg/g b.d.l. n.d. b.d.l.
2RSD % barite line C (32μm, 2J/cm ² , 10H2) 2RSD % barite line C (32μm, 2J/cm ² , 10H2) 2RSD % barite line C (32μm, 2J/cm ² , 10H2)	ku µg/g b.d.l. 99 b.d.l. n.d.	Rh µg/g b.d.l. n.d. b.d.l. n.d.	Pd μg/g n.d. n.d. n.d. b.d.l.	Ag µg/g n.d. b.d.l. n.d. b.d.l.	Cd μg/g b.d.l. n.d. n.d. b.d.l.	n.d. b.d.l. b.d.l. b.d.l.	Sn µg/g b.d.l. b.d.l. n.d. 0.2	Sb(121) Sb µg/g b.d.l. n.d. b.d.l. b.d.l.	Te(125) <u>Te μg/g</u> b.d.l. n.d. n.d. n.d.	Te(128) Te μg/g n.d. n.d. n.d. n.d.	Cs(133) Cs µg/g 0.3 52 0.3 53 0.2 56 0.3	Ba(135) Ba µg/g 599113 8 585229 8 597056 8 591014	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 571165	Sm (147) Sm µg/g n.d. n.d. n.d. n.d.	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. n.d.	Tb μg/g n.d. n.d. b.d.l. n.d.	Dy μg/g b.d.l. n.d. b.d.l. b.d.l.
Jance Inte A (32µm, 2)/cm ² , 10H2) 2RSD % barite line B (32µm, 2)/cm ² , 10H2) 2RSD % barite line C (32µm, 2)/cm ² , 10H2) 2RSD % barite line D (32µm, 2)/cm ² , 10H2) 2RSD %	ku µg/g b.d.l. 99 b.d.l. n.d. 	Rh µg/g b.d.l. n.d. b.d.l. n.d. 	Pd μg/g n.d. n.d. n.d. b.d.l.	Ag μg/g n.d. b.d.l. n.d. b.d.l. 	Cd μg/g b.d.l. n.d. n.d. b.d.l.	n.d. b.d.l. b.d.l. b.d.l. b.d.l.	Sn µg/g b.d.l. b.d.l. n.d. 0.2 93	Sb(121) Sb µg/g b.d.l. n.d. b.d.l. b.d.l. 	Te(125) <u>Te μg/g</u> b.d.l. n.d. n.d. n.d.	Te(128) Te μg/g n.d. n.d. n.d. n.d.	Cs(133) Cs µg/g 0.3 52 0.3 53 0.2 56 0.3 40	Ba(135) Ba µg/g 599113 8 585229 8 597056 8 591014 8	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 571165 7	Sm (147) Sm µg/g n.d. n.d. n.d. n.d. 	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. n.d. n.d.	тв(159) <u>Tb µg/g</u> n.d. n.d. b.d.l. n.d. 	Dy μg/g b.d.l. n.d. b.d.l. b.d.l.
JarsD % barite line B (32μm, 2J/cm ² , 10H2) ZRSD % barite line B (32μm, 2J/cm ² , 10H2) ZRSD % barite line D (32μm, 2J/cm ² , 10H2) ZRSD % barite line E (32μm, 2J/cm ² , 10H2) ZRSD %	ku µgyg b.d.l. 99 b.d.l. n.d. b.d.l.	Rh µg/g b.d.l. n.d. b.d.l. n.d. n.d. 	Pd μg/g n.d. n.d. n.d. b.d.l. n.d. n.d. 	Ag μg/g n.d. b.d.l. n.d. b.d.l. n.d. n.d. 	Cd μg/g b.d.l. n.d. n.d. b.d.l. n.d. n.d. 	in μg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l.	Sn µg/g b.d.l. b.d.l. n.d. 0.2 93 b.d.l. 	Sb(121) Sb µg/g b.d.l. n.d. b.d.l. b.d.l. n.d. 	Te(125) <u>Te µg/g</u> b.d.l. n.d. n.d. b.d.l. 	Te(128) Te μg/g n.d. n.d. n.d. n.d. b.d.l. 	Cs(133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 591014 8 587109 8	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 574770 7 574165 7 594443 7	Sm (147) Sm μg/g n.d. n.d. n.d. n.d. 0.3 65	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. n.d. b.d.l.	Tb µg/g n.d. n.d. b.d.l. n.d. n.d. 	Dy μg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l.
Jans M (32μm, 2)/cm ² , 10H2) JRSD % barite line B (32μm, 2]/cm ² , 10H2) ZRSD % barite line C (32μm, 2]/cm ² , 10H2) ZRSD % barite line E (32μm, 2]/cm ² , 10H2) ZRSD % barite line F (32μm, 2]/cm ² , 10H2) ZRSD %	ku µgyg b.d.l. 99 b.d.l. n.d. b.d.l. b.d.l.	<u>Rh μg/g</u> b.d.l. n.d. n.d. n.d. b.d.l. 	Pd µg/g n.d. n.d. b.d.l. n.d. n.d. n.d. 	Ag µg/g n.d. b.d.l. n.d. b.d.l. n.d. n.d. 	<u>Cd μg/g</u> b.d.l. n.d. b.d.l. b.d.l. b.d.l.	n.(125) n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	Sn μg/g b.d.l. b.d.l. n.d. 93 b.d.l. n.d. 	Sb(121) Sb µg/g b.d.l. n.d. b.d.l. n.d. b.d.l. b.d.l. 	Te(125) <u>Te μg/g</u> b.d.l. n.d. n.d. b.d.l. n.d. n.d. 	Te(128) <u>Te μg/g</u> n.d. n.d. n.d. b.d.l. n.d. n.d. 	Cs(133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48 0.5 41	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597034 8 597034 8 597034 8 597034 8 597034 8 597035 8 597035 8 597035 8 597035 8 597056 8 597035 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 597056 597056 597056 507056 8 507056 8 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507056 507050 507056 50705555555555	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 574770 7 574770 7 594443 7 594443 7 582290 7	Sm(147) Sm μg/g n.d. n.d. n.d. 0.3 65 n.d. 	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. 	Tb(159) Tb μg/g n.d. b.d.l. n.d. n.d. n.d. n.d. 	Dy µg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jance line A (32µm, 2)/cm ² , 10H2) 2RSD % barite line B (32µm, 2)/cm ² , 10H2) 2RSD % barite line C (32µm, 2)/cm ² , 10H2) 2RSD % barite line E (32µm, 2)/cm ² , 10H2) 2RSD % barite line F (32µm, 2)/cm ² , 10H2) 2RSD % barite line G (32µm, 2)/cm ² , 10H2)	ku pg/g b.d.l. 99 b.d.l. n.d. b.d.l. b.d.l. n.d.	<u>Rh μg/g</u> b.d.l. n.d. b.d.l. n.d. b.d.l. b.d.l.	Pd µg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d.	Ag µg/g n.d. b.d.l. h.d.l. b.d.l. n.d. n.d. n.d.	Cd µg/g b.d.l. n.d. b.d.l. n.d. b.d.l. b.d.l. n.d.	n.(125) n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d.	Sn μg/g b.d.l. b.d.l. 0.2 93 b.d.l. n.d. n.d. b.d.l.	Sb(121) Sb µg/g b.d.l. b.d.l. b.d.l. n.d. b.d.l. n.d.	Te(125) <u>Te μg/g</u> b.d.l. n.d. n.d. b.d.l. b.d.l.	Te(128) <u>Te μg/g</u> n.d. n.d. n.d. b.d.l. b.d.l.	Cs(133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48 0.5 41 0.5 41 0.5	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 597056 8 591014 8 587109 8 594338 10 604267	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 574770 7 594443 7 594443 7 594443 7 594443 7 5944631	Sm(147) Sm μg/g n.d. n.d. n.d. 0.3 65 n.d. b.d.l.	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	Tb μg/g n.d. b.d.l. n.d. n.d. n.d. n.d. n.d.	Dy µg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jarte line A (32µm, 21/cm ² , 10H2) JRSD % barite line B (32µm, 21/cm ² , 10H2) ZRSD % barite line C (32µm, 21/cm ² , 10H2) ZRSD % barite line E (32µm, 21/cm ² , 10H2) ZRSD % barite line F (32µm, 21/cm ² , 10H2) ZRSD % barite line G (32µm, 21/cm ² , 10H2) ZRSD % barite line G (32µm, 21/cm ² , 10H2)	k (pg/g b.d.l. 0.5 99 b.d.l. n.d. b.d.l. b.d.l. n.d. 	Rh μg/g b.d.l. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. b.d.l. n.d. 0.1	Pd µg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. 	Ag µg/g n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. h.d.	Cd µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. b.d.l. 	n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	Sn µg/g b.d.l. b.d.l. n.d. 93 b.d.l. n.d. b.d.l. b.d.l.	Sb(121) Sb µg/g b.d.l. h.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. n.d.	Te(125) Te μg/g b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l.	Te(128) <u>Te μg/g</u> n.d. n.d. n.d. b.d.l. b.d.l. 2.6	Cs(133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48 0.5 41 0.4 41 0.4	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 597056 8 597056 8 597014 8 5971014 8 594338 10 604267 8 505060	Ba(137) Ba µg/g 599290 7 569107 7 574770 7 574770 7 594443 7 594443 7 582290 7 594681 7 594681 7	Sm(14/) Sm µg/g n.d. n.d. n.d. 0.3 65 n.d. b.d.l. b.d.l. 	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	Tb μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. 	Dy µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jarite line A (32µm, 2)/cm ² , 10H2) 2RSD % barite line B (32µm, 2)/cm ² , 10H2) 2RSD % barite line C (32µm, 2)/cm ² , 10H2) 2RSD % barite line E (32µm, 2)/cm ² , 10H2) 2RSD % barite line F (32µm, 2)/cm ² , 10H2) 2RSD % barite line G (32µm, 2)/cm ² , 10H2) 2RSD %	ki pg/g b.d.l. 99 b.d.l. b.d.l. b.d.l. n.d. n.d. 	Rh μg/g b.d.l. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. 0.1 79	Pd μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. 	Ag yeg (g n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. b.d.l. b.d.l.	Ccd µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. n.d. 	In yergs n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. 	Sn µg/g b.d.l. b.d.l. 0.2 93 b.d.l. n.d. n.d. b.d.l. b.d.l.	Sb(121) Sb µg/g b.d.l. h.d.l. b.d.l. n.d. b.d.l. n.d. n.d. n.d. 	Te(125) Te μg/g b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. 	Te(128) <u>Te μg/g</u> n.d. n.d. n.d. b.d.l. n.d. b.d.l. p.d. 2.6 94	Cs (133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48 0.5 41 0.4 41 0.4 41 0.4 34	Ba(135) Ba µg/g 599113 8 585229 8 597056 8 591014 8 591014 8 594338 10 604267 8 595960 8	Ba(137) Ba µg/g 5992290 7 559107 7 574770 7 574165 7 594443 7 594443 7 594681 7 594681 7 594681 7 594681 7	Sm(147) Sm µg/g n.d. n.d. n.d. 0.3 65 n.d. b.d.l. b.d.l. n.d. 	Gd(157) Gd µg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. 	Tb(159) Tb(159) n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. 	Dy µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jante line A (32µm, 21/cm ² , 10H2) JRSD % barite line B (32µm, 21/cm ² , 10H2) ZRSD % barite line C (32µm, 21/cm ² , 10H2) ZRSD % barite line E (32µm, 21/cm ² , 10H2) ZRSD % barite line F (32µm, 21/cm ² , 10H2) ZRSD % barite line G (32µm, 21/cm ² , 10H2) ZRSD % barite line H (32µm, 21/cm ² , 10H2) ZRSD %	b.d.l. 0.5 99 b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. b.d.l.	Rh μg/g b.d.l. n.d. b.d.l. b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. 0.1 79	Pd μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d.	Ag µg/g n.d. b.d.l. b.d.l. n.d. n.d. b.d.l. b.d.l.	Cd µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. 	In yerg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d.	Sn µ/160 Sn µg/g b.d.l. b.d.l. 0.2 93 b.d.l. n.d. b.d.l. b.d.l. b.d.l.	Sb(121) Sb µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. 	Te(125) Te μg/g b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l.	Te(128) Te µg/g n.d. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. 2.6 94	Cs (133) Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 48 0.5 41 0.4 41 0.4 34	Ba(135) Ba µg/g 599113 8 585229 8 597056 8 591014 8 591014 8 594338 10 604267 8 595960 8	Ba(137) Ba µg/g 5992290 7 569107 7 574770 7 574165 7 594443 7 594443 7 594681 7 594681 7 626983 7 626983 7	Sm(14/) Sm µg/g n.d. n.d. n.d. n.d. 0.3 65 n.d. b.d.l. b.d.l. s.d.	Gd(157) Gd(µg/g n.d. b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. b.d.l. b.d.l.	Tb (159) Tb µg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d.	Dy µg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jarite line A (32µm, 21/cm ² , 10H2) JRSD % barite line B (32µm, 21/cm ² , 10H2) ZRSD % barite line C (32µm, 21/cm ² , 10H2) ZRSD % barite line D (32µm, 21/cm ² , 10H2) ZRSD % barite line F (32µm, 21/cm ² , 10H2) ZRSD % barite line G (32µm, 21/cm ² , 10H2) ZRSD % barite line H (32µm, 21/cm ² , 10H2) ZRSD % Standards NUSTE12	ku μg/g b.d.l. 0.5 99 b.d.l. n.d. b.d.l. b.d.l. n.d. Ru μg/g	Rh μg/g b.d.l. n.d. b.d.l. n.d. b.d.l. n.d. b.d.l. 0.d. 79 Rh μg/g	Pd μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. Pd μg/g	Ag µg/g n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. b.d.l. Ag µg/g	Cd µg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. Cd µg/g	In μg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. n.d. 	Sn μg/g b.d.l. b.d.l. 0.2 93 b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. Sn μg/g	Sb(121) Sb.gg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. Sb.d.l. Sb.gg/g 2-	Te(125) Te μg/g b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. Te μg/g	Te μg/g n.d. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. 2.6 94	Cs μg/g Cs μg/g 0.3 52 0.3 53 0.2 56 0.3 40 0.4 41 0.4 41 0.4 34 Cs μg/g 22	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 591014 8 594338 10 604267 8 594338 10 604267 8 595960 8 595960 8 Ba μg/g	Ba (μg/g 599290 7 569107 7 574700 7 574165 7 594443 7 594681 7 594681 7 594681 7 626983 7 8 20	Sm(14/) Sm μg/g n.d. n.d. n.d. n.d. n.d. b.d.l. b.d.l. Sm μg/g	Gd (157) Gd µg/g n.d. b.d.l. n.d. b.d.l. b.d.l. b.d.l. d.d. Gd µg/g	Tb μg/g n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. Tb μg/g	b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jante line A (32µm, 21/cm ² , 10H2) ZRSD % barite line B (32µm, 21/cm ² , 10H2) ZRSD % barite line C (32µm, 21/cm ² , 10H2) ZRSD % barite line D (32µm, 21/cm ² , 10H2) ZRSD % barite line F (32µm, 21/cm ² , 10H2) ZRSD % barite line G (32µm, 21/cm ² , 10H2) ZRSD % barite line H (32µm, 21/cm ² , 10H2) ZRSD % Standards NIST612 NIST612	ku μg/g b.d.l. 0.5 99 b.d.l. n.d. b.d.l. n.d. Ru μg/g n.d. Ru μg/g n.d.	Rh μg/g b.d.l. n.d. b.d.l. b.d.l. n.d. 1	Pd μg/g n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.	Ag µg/g n.d. b.d.l. n.d. n.d. n.d. n.d. b.d.l. h.d.l. h.d.l. h.d.l. 22 251	Cd μg/g b.d.l. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. cd μg/g 28 270	In μg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. η.d. η.d. 	Sn μg/g Sn μg/g b.d.l. n.d. 93 b.d.l. b.d.l. b.d.l. b.d.l. Sn μg/g 39 430	Sb(121) Sb µg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. Sb µg/g 35 206	Te(125) Te μg/g b.d.l. n.d. n.d. b.d.l. b.d.l. b.d.l. Te μg/g n.d. 302	Te(128) Te μg/g n.d. n.d. n.d. b.d.l. b.d.l. b.d.l. Σ.6 94 Te μg/g n.d. 302	Cs μg/g Cs μg/g Cs μg/g Cs μg/g Cs μg/g A3 Cs μg/g A3 Cs μg/g A3 A3 A3 A3 A3 A3 A3 A3 A3 A3	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 591014 8 591014 8 591014 8 594338 10 604267 8 594338 10 604267 8 595960 8 8 595960 8 8 595960 8 8 595960 8 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 59505 8 59505 8 59505 8 59505 8 59505 8 59505 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 59500 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 595000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 505000 8 50000 8 500000 8 500000 8 500000 8 500000 8 50000000 8 500000000	Ba(137) Ba µg/g 599290 7 5590290 7 574077 7 574077 7 571165 7 594443 7 582290 7 594681 7 626983 7 882 µg/g 39 452	Sm(14/) Sm μg/g n.d. n.d. n.d. n.d. 0.3 65 n.d. b.d.l. n.d. Sm μg/g 38 453	Gd(157) Gd μg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. gd μg/g 37 4/3	Tb μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. Tb μg/g 38 437	Dy μg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.
Jante line A (32µm, 21/cm ² , 10H2) 2RSD % barite line B (32µm, 21/cm ² , 10H2) 2RSD % barite line C (32µm, 21/cm ² , 10H2) 2RSD % barite line E (32µm, 21/cm ² , 10H2) 2RSD % barite line F (32µm, 21/cm ² , 10H2) 2RSD % barite line G (32µm, 21/cm ² , 10H2) 2RSD % barite line H (32µm, 21/cm ² , 10H2) 2RSD % Standards NIST612 NIST610_611 PGF NI7D	ku μg/g b.d.l. 0.5 99 b.d.l. n.d. b.d.l. n.d. Ru μg/g n.d. Ru μg/g n.d. 37	Rh μg/g b.d.l. n.d. b.d.l. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d.	Pd μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η. η. η. η. η. η. η. η. η. η. η. η. η. η.	Ag μg/g n.d. b.d.l. n.d. n.d. n.d. b.d.l. b.d.l. b.d.l. b.d.l. β.d.l. β.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. h.d. 	Cd μg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. n.d. n.d. cd μg/g 28 28 270 	In μg/g n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. n.d. n.d. 39 434	Sn μg/g b.d.l. b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. 	Sb(121) Sb µg/g b.d.l. b.d.l. b.d.l. n.d. b.d.l. n.d. s.d.l. Sb µg/g 355 3366 -	Te (µ25) Te μg/g b.d.l. n.d. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. 	Te(128) Te μg/g n.d. n.d. n.d. b.d.l. b.d.l. b.d.l. 2.6 94 Te μg/g n.d. 302	Cs μg/g Cs μg/g Cs μg/g Cs μg/g Cs μg/g 43 366 - - - - - - - - - - - - -	Ba(135) Ba μg/g 599113 8 585229 8 597056 8 597056 8 597014 8 597014 8 597014 8 597014 8 594338 10 604267 8 595960 8 8 595960 8 8 595960 8 8 595960 8 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 597056 8 59559 8 5959956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595956 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595950 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595960 8 595950 8 595950 8 595950 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 595050 8 505050 8 505050 8 505050 8 505050 8 505050 8 505050 8 5050500 8 50	Ba(137) Ba μg/g 599290 7 559107 7 574770 7 574770 7 594443 7 5944681 7 594681 7 626983 7 894681 7 8394681 7 8394681 7 626983 7	Sm(14/) Sm μg/g n.d. n.d. n.d. 0.3 65 n.d. b.d.l. b.d.l. Sm μg/g 38 453 	Gd μg/g Gd μg/g Gd μg/g 37 449 	Tb μg/g n.d. n.d. b.d.l. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η.d. η. η. η. η. η. η. η. η. η. η. η. η. η.	Dy μg/g b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.

1044 Table S3 (cont.):

	Ho(165)	Er(166)	Tm(169)	Yb(172)	Lu(175)	Ta(181)	W(182)	Re(185)	Os(189)	lr(193)	Pt(195)	Au(197)	TI(205)	Pb(208)	Bi(209)	Th(232)	U(238)
	Ho µg/g	Er µg/g	Tm µg/g	Yb µg/g	Lu µg/g	Ta µg/g	W μg/g	Re µg/g	Os, μg/g	Ir μg/g	Pt µg/g	Au μg/g	Tl μg/g	Pb µg/g	Bi µg/g	Th µg/g	U μg/g
barite line A (32µm, 2J/cm², 10Hz)	b.d.l.	b.d.l.	n.d.	b.d.l.	0.0	b.d.l.	n.d.	b.d.l.	n.d.	b.d.l.	b.d.l.	b.d.l.	n.d.	3.1	b.d.l.	n.d.	b.d.l.
2RSD %					71									32			
barite line B (32µm, 2J/cm², 10Hz)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.1	n.d.	n.d.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	8.0	n.d.	b.d.l.	b.d.l.
2RSD %					72									28			
barite line C (32µm, 2J/cm ² , 10Hz)	b.d.l.	b.d.l.	n.d.	b.d.l.	0.0	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.9	b.d.l.	n.d.	n.d.
2RSD %					98									31			
barite line D (32µm, 2J/cm², 10Hz)	b.d.l.	n.d.	n.d.	b.d.l.	n.d.	n.d.	n.d.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	n.d.	3.4	n.d.	b.d.l.	b.d.l.
2RSD %														23			
barite line E (32µm, 2J/cm², 10Hz)	b.d.l.	b.d.l.	b.d.l.	n.d.	0.0	n.d.	n.d.	n.d.	n.d.	b.d.l.	n.d.	b.d.l.	n.d.	2.9	0.0	b.d.l.	0.0
2RSD %					79									29	82		94
barite line F (32µm, 2J/cm ² , 10Hz)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.0	n.d.	b.d.l.	b.d.l.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2.0	n.d.	n.d.	b.d.l.
2RSD %					87									24			
barite line G (32µm, 2J/cm ² , 10Hz)	b.d.l.	n.d.	n.d.	n.d.	0.0	n.d.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.2	n.d.	n.d.	b.d.l.
2RSD %					70									34			
barite line H (32µm, 2J/cm ² , 10Hz)	b.d.l.	b.d.l.	n.d.	b.d.l.	n.d.	b.d.l.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.6	b.d.l.	b.d.l.	b.d.l.
2RSD %														33			
Standards	Ho µg/g	Er µg/g	Tm μg/g	Yb µg/g	Lu µg/g	Ta µg∕g	W μg/g	Re µg/g	Os, μg/g	Ir μg/g	Pt μg/g	Au µg/g	Tl µg∕g	Pb µg/g	Biµg/g	Th µg/g	U μg/g
NIST612	38	38	37	39	37	38	38	7	n.d.	0.0	3	5	15	39	30	38	37
NIST610_611	449	455	435	450	439	446	444	50	n.d.	n.d.	3	24	60	426	384	457	462
PGE_Ni7b	-	-	-	-	-	-	-	55	85	54	33	-	-	-	-	-	-

1046 Strontium isotope laser ablation analysis

1047 In-situ Sr isotope analyses including data reduction using the linear regression slope (LRS)

1048 method followed a previously published procedure initially developed for carbonates (Fietzke

1049 et al., 2008). For barite, the former method had to be modified slightly with respect to cup

1050 configuration and correction of isobaric interferences. The cup configuration used is provided

in Table S4.

1045

1052 Table S4: Cup configuration for LA-MC-ICPMS Sr isotope analyses in barite samples. For all

1053 atomic mass units (amu) monitored the relative abundances (in %) of isotope of interest and

1054 isobaric interferences are provided.

Сир	amu	Sr	Kr	Rb	BaAr ²⁺	Er ²⁺	Yb ²⁺	Lu ²⁺	Hf ²⁺
L4	83		11.4953			33.61			
L3	83.5					22.93			
L2	85			72.1654	0.1058	14.93	3.04		
L1	86	9.8566	17.2984		0.1012		21.83		
AX	86.5						16.13		
H1	87	7.0015		27.8346	2.417		31.83		0.162
H2	87.5				6.592			97.416	
H3	88	82.5845			7.853		12.76	2.584	5.2604
H4	88.5				11.232				18.5953

- 1056 In accordance with the results of elemental analyses using LA-ICPMS (Table S2) no significant
- 1057 contribution from doubly-charged REE ions could be found. The same is true for Hf, thus no
- 1058 correction for this group of elements was required.
- 1059 Nevertheless, significant signal intensities on 87.5 amu and 88.5 amu occur during ablation of
- 1060 barite samples but are perfectly absent while ablating carbonates. Both contributions are
- 1061 strongly correlated (R²=0.999995) yielding an 87.5/88.5 ratio of 0.5817 when evaluating all
- 1062 barite data. The latter observation points towards an interferences consisting of doubly-
- charged BaAr cluster ions (unfractionated ratio of ¹³⁵Ba⁴⁰Ar²⁺/¹³⁷Ba⁴⁰Ar²⁺=0.5869). Based on the
 measured 88.5 intensity using the respective Ba isotope abundances, intensities measured on
- 1065 86, 87 and 88 amu have been corrected for the contribution from BaAr²⁺. For all barite samples
- 1066 this is by far the dominant interference correction. Changing Kr contributions to 86 amu had
- 1067 been monitored using 83 amu and were found to be insignificant. Due to the practical absence
- 1068 of Rb in the barite samples (see Table S2) the correction on 87 amu (⁸⁷Rb contribution) was also
- 1069 insignificant.
- 1070 The reported ⁸⁷Sr/⁸⁶Sr results (Table 4) were calculated by applying the BaAr²⁺ correction and
- 1071 the mass bias correction (exponential law; based on ⁸⁶Sr/⁸⁸Sr=0.1194). The in-situ data are in
- 1072 good agreement with the bulk analyses ⁸⁶Sr/⁸⁸Sr results (Table 3), thus supporting the
- 1073 application of the $BaAr^{2+}$ correction.

ALV2467-R2		ALV2464-R4		ALV2464-R4 (amorph. silica		
THomogenization	T _{Trapping}	T _{Homogenization}	T _{Trapping}	T _{Homogenization}	T _{Trapping}	
114	124	121	131	118	128	
116	126	123	133	120	130	
128	138	125	135	120	130	
130	141	125	135	124	134	
130	141	126	136	127	137	
131	142	126	136			
133	144	126	136			
140	151	126	136			
147	158	133	144			
152	163	134	145			
155	166	135	146			
157	168	135	146			
160	172	135	146			
172	184	138	149			
173	185	142	153			
174	186	147	158			
174	186	161	173			
182	194	172	184			
183	195	173	185			
190	203	178	190			
195	208	183	195			
196	209	184	196			
196	209	191	204			
209	222	193	206			
214	227	216	229			
214	227	221	234			
218	231	222	235			
220	233	223	236			
229	242	223	236			
240	253	257	271			
243	256	266	280			
258	272	269	283			
Average	181		189		132	
Std. Dev.	47		41		4	

1075 Table S5: Fluid inclusion homogenization and trapping temperatures: