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**Noble gases in sulfide deposits of modern deep-sea hydrothermal systems:  
Implications for heat fluxes and hydrothermal fluid processes**

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23 **ABSTRACT**

24 Studies of noble gases in seafloor sulfide deposits are an important tool for  
25 understanding the origin of ore-forming fluids, both enabling the determination of  
26 noble gas sources and revealing the degree of fluid-rock interaction and mantle  
27 degassing. The noble gas concentrations and isotopic compositions of 27 sulfide, 3  
28 sulfate, and 2 opal mineral aggregate samples have been studied in different  
29 hydrothermal fields from the East Pacific Rise, Mid-Atlantic Ridge, Central Indian  
30 Ridge, Southwest Indian Ridge, and North Fiji Back-Arc Basin. The helium  
31 concentrations and isotopic ratios in the sulfide aggregate samples are variable ( $^4\text{He}$   
32  $0.12$  to  $22 \times 10^{-8}$   $\text{cm}^3$  STP/g;  $^3\text{He}/^4\text{He} \sim 0.6$  to  $10.4$   $R_a$ ), and most of the sulfide helium  
33 concentrations are higher than those in the opal mineral samples ( $^4\text{He}$   $0.017$  and  $0.028$   
34  $\times 10^{-8}$   $\text{cm}^3$  STP/g), suggesting that the low-temperature fluids have lost their mantle  
35 helium during cooling. The helium of high ( $> 7$   $R_a$ ), medium ( $1-7$   $R_a$ ), and low ( $\approx 1$   
36  $R_a$ )  $^3\text{He}/^4\text{He}$  ratio samples is derived mainly from the MORB or OIB mantle by  
37 magma degassing, from mixing between hydrothermal fluid and seawater during  
38 ore-forming processes, and from ambient seawater, respectively. The high  $^3\text{He}/^4\text{He}$   
39 ratios ( $> 7$   $R_a$ ) of sulfides imply that high-temperature sulfides retain the helium  
40 isotopic compositions of the primary hydrothermal fluid, whereas low-temperature  
41 sulfides, sulfates, and opal minerals do not.

42 The neon, argon, krypton, and xenon concentrations in the sulfide aggregate samples  
43 are also variable; in most of the sulfide aggregates, they are significantly lower than in  
44 the sulfate and opal mineral samples. It is known that barite and opal minerals are

45 characteristic of low-temperature ( $< 200^{\circ}\text{C}$ ) paragenetic associations, indicating that  
46 heavier noble gases (Ne, Ar, Kr and Xe) are enriched under low-temperature  
47 conditions. Most of the sulfide, sulfate and opal mineral aggregate samples possess  
48 heavy noble gas elemental abundances similar to those of air-saturated seawater and  
49 Ne, Ar, and Xe isotopic compositions that span narrow ranges around atmospheric  
50 values, an observation which is most easily explained by the dominance of a  
51 seawater-derived component.

52 In addition, based on the calculated helium/heat ratios, global helium and heat fluxes  
53 to high-temperature hydrothermal vents are approximately  $0.05\text{--}6 \times 10^4$  kg per year  
54 and  $0.1\text{--}12 \times 10^{12}$  W, meaning that roughly 0.3% of ocean heat is supplied by seafloor  
55 high-temperature hydrothermal activity.

56 **Keywords:** noble gases; massive sulfides; sulfates; opal; seafloor hydrothermal  
57 systems

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67 **1. Introduction**

68 The study of noble gases in seafloor hydrothermal sulfides is key to revealing the  
69 evolution of seafloor hydrothermal systems. Such studies can be used to reconstruct  
70 fluid temporal variability and to extend our knowledge of the helium/heat ratio back  
71 into the geological record (e.g., Turner and Stuart, 1992; Stuart et al., 1994a, b;  
72 Jean-Baptiste and Fouquet, 1996; Zeng et al., 2001, 2004). To date, noble gas studies  
73 have been performed in sulfide deposits of modern seafloor hydrothermal fields in the  
74 Middle Valley of the northern Juan de Fuca Ridge (NJdFR) (Stuart et al., 1994a, b); in  
75 the Trans-Atlantic Geotraverse (TAG) and Snake Pit hydrothermal fields of the  
76 Mid-Atlantic Ridge (MAR) (Stuart et al., 1994b; Zeng et al., 2001); in the East Pacific  
77 Rise (EPR) near 13°N (Stuart et al., 1995; Jean-Baptiste and Fouquet, 1996) and 21°N  
78 (Turner and Stuart, 1992; Stuart et al., 1994b); in the JADE hydrothermal field of the  
79 Okinawa Trough (Zeng et al., 2004; Hou et al., 2005; Lüders and Niedermann, 2010);  
80 in the North Fiji Basin (NFB) (Lüders and Niedermann, 2010); and in the  
81 PACMANUS hydrothermal field of the Manus Basin in Papua New Guinea (Webber  
82 et al., 2011). The  $^3\text{He}/^4\text{He}$  ratios of sulfide-, sulfate-, and opal-hosted fluid inclusions  
83 from the Middle Valley, the EPR near 13°N and 21°N, the TAG, Snake Pit, JADE,  
84 NFB, and PACMANUS hydrothermal fields range from 0.29 to 13.3  $R_a$  (sulfide  
85 samples, n=96;  $R_a$  is the atmospheric  $^3\text{He}/^4\text{He}$  ratio of  $1.39 \times 10^{-6}$ ) and from 2.6 to 12.4  
86  $R_a$  (sulfate and opal samples, n=16), respectively (Turner and Stuart, 1992; Stuart et  
87 al., 1994a, 1994b, 1995; Jean-Baptiste and Fouquet, 1996; Zeng et al., 2001, 2004;  
88 Hou et al., 2005; Lüders and Niedermann, 2010; Webber et al., 2011). Most of these

89 values are almost indistinguishable from the  $^3\text{He}/^4\text{He}$  ratios of vent fluids (5.3–8.3 Ra)  
90 from these hydrothermal fields (e.g., Lupton et al., 1980; Craig and Lupton, 1981;  
91 Kim et al., 1984; Kennedy, 1988; Kodera et al., 1988; Jean-Baptiste et al., 1991;  
92 Rudnicki and Elderfield, 1992; Charlou et al., 1996) and of MOR basalts (6–11 Ra)  
93 (Kurz et al., 1982; Graham, 2002), suggesting that helium is predominantly derived  
94 from a magmatic source beneath the hydrothermal systems (Zeng et al., 2004; Hou et  
95 al., 2005; Lüders and Niedermann, 2010). This shows that the fluid inclusions of  
96 sulfides reliably record the helium isotope ratio of the original hydrothermal fluid  
97 (Lüders and Niedermann, 2010). In the Middle Valley, the  $^3\text{He}/^4\text{He}$  ratios (5.8–7.1 Ra)  
98 of fluid inclusions in sulfide minerals are lower than those of typical MOR vent fluids  
99 (~8 Ra; e.g., Craig and Lupton, 1981; Kennedy, 1988; Kodera et al., 1988) and are  
100 closer to those of vent fluids from the sediment-covered Guaymas basin (7 Ra; Lupton,  
101 1983), suggesting a contribution of radiogenic He derived either from sedimentary  
102 pore fluids or from aging of the magmatic system beneath the NJdFR (Stuart et al.,  
103 1994a). The fluid-inclusion  $^3\text{He}/^4\text{He}$  ratios of sulfides reflect a mixture of  
104 basalt-derived He and radiogenic He acquired from pore fluids in the overlying  
105 Pleistocene turbidite sediments after seawater-basalt interaction, and the He isotopes  
106 can be used to distinguish pore fluids from seawater in seafloor hydrothermal systems  
107 (Stuart et al., 1994b). In another study, the helium isotopic compositions of  
108 fluid-inclusions in hydrothermal sulfides from the EPR near 13°N were measured  
109 using both crushing and heating techniques, and comparison of the two extraction  
110 methods suggests that both techniques give similar results (Jean-Baptiste and Fouquet,

111 1996).

112 The elemental abundances of Ne, Ar, Kr, and Xe in fluid inclusions of sulfide samples  
113 from the JADE hydrothermal field and NFB suggest that the heavier noble gases are  
114 derived from ambient seawater (Zeng et al., 2004; Lüders and Niedermann, 2010).  
115 The Ar, Kr, and Xe concentrations of Middle Valley sulfides are 10 to 50 times higher  
116 than those of sulfides from the EPR near 21°N, and the Ar and Xe isotopic ratios of  
117 sulfides from both settings are indistinguishable from atmospheric values (Turner and  
118 Stuart, 1992). The argon isotopic ratios in fluid inclusions of sulfides from the TAG  
119 ( $^{40}\text{Ar}/^{36}\text{Ar}$  287–359; Zeng et al., 2001) and the PACMANUS hydrothermal field  
120 ( $^{40}\text{Ar}/^{36}\text{Ar}$  295–310; Webber et al., 2011) are somewhat more variable, but still close  
121 to the atmospheric ratio (295.5 after Nier, 1950; 298.56 after Lee et al., 2006; Mark et  
122 al., 2011). This also indicates that most of the heavier noble gases come from seawater  
123 (Turner and Stuart, 1992; Zeng et al., 2001; Webber et al., 2011). Likewise,  $^{40}\text{Ar}$   
124 excesses of up to 2.6% relative to atmospheric Ar (i.e.,  $^{40}\text{Ar}/^{36}\text{Ar}$  up to 303) are  
125 present in fluid inclusions of sulfide samples from the EPR near 13°N. Fluid-inclusion  
126  $^3\text{He}/^4\text{He}$  ratios of 7.3–9.3  $R_a$  in the same samples are typical for mid-ocean ridge  
127 hydrothermal fluids and imply a mantle origin for the  $^{40}\text{Ar}$  excess also (Stuart and  
128 Turner, 1998).

129 Although noble gases in seafloor hydrothermal sulfides can provide important  
130 information on fluid sources, fluid flux changes (e.g., Turner and Stuart, 1992), and  
131 hydrothermal processes (e.g., Stuart et al., 1994a, b), noble gas composition data for  
132 fluid inclusions in sulfide, sulfate, and opal samples from seafloor hydrothermal

133 systems in mid-ocean ridge (MOR) and back-arc basin (BAB) settings are still scarce;  
134 in particular, Ne, Ar, Kr, and Xe data for modern seafloor sulfide deposits are lacking.  
135 In this study, noble gas concentrations and isotopic compositions have been measured,  
136 for the first time, in seafloor hydrothermal sulfide deposits from the EPR near 1-2°S,  
137 the Logatchev hydrothermal field (LHF) in the MAR near 15°N, the MAR near 13°S,  
138 the Central Indian Ridge (CIR), and the Southwest Indian Ridge (SWIR) (Fig. 1). The  
139 characteristics of noble gas concentrations and isotopic compositions in sulfide,  
140 sulfate, and opal mineral aggregates are described, seawater and magmatic noble gas  
141 contributions are characterized, the implications for fluid-rock interaction and  
142 fluid-seawater mixing are explored, and helium and heat fluxes from hydrothermal  
143 fluids to seafloor hydrothermal sulfide deposits are evaluated.

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155 **2. Sampling and methods**

156 Seafloor hydrothermal sulfide samples were recovered by TV-grab samplers from the  
157 fast-spreading EPR near 13°N, the ultra-fast spreading EPR near 1-2°S, the Kairei  
158 hydrothermal field (KHF) and the Edmond hydrothermal field (EHF) on the  
159 intermediate-spreading CIR near 25°S, the slow-spreading MAR near 13°S and at the  
160 LHF (15°N), and the ultra-slow spreading SWIR near 63.5°E and in the “A” area  
161 (49°E) in 2005, 2007, 2008, 2009, and 2010 during the DY105-17, DY115-19,  
162 DY115-20, and DY115-21 cruises of R/V “Dayang Yihao”. Sulfide samples from the  
163 Sonne 99 hydrothermal field (S99HF) in the back-arc North Fiji Basin (NFB) were  
164 collected in 1998 during the SO134 cruise of HYFIFLUX II (Fig. 1).

165 At the EPR near 13°N and 1-2°S, the KHF, the EHF, the MAR near 13°S, the A area,  
166 the SWIR near 63.5°E, and the S99HF, the seafloor hydrothermal sulfides are hosted  
167 by mid-ocean ridge basalt (MORB) (e.g., Zeng et al., 2010, 2014). The KHF is  
168 situated on basaltic rocks but the hydrothermal fluids also interact with and circulate  
169 through ultramafic rocks (Nakamura et al., 2009). In the LHF, the hydrothermal  
170 sulfide deposit is associated with ultramafic rocks located in a debris flow consisting  
171 of heterogeneous ultramafic and mafic intrusive rocks, including serpentinized  
172 harzburgite, serpentinized dunite, gabbonorite, and olivine-bearing basalt (e.g.,  
173 Petersen et al., 2009; Zeng et al., 2014). Figure 1 and Table 1 give information about  
174 the sampling location, depth, and mineralogy of hydrothermal sulfide samples.  
175 Seafloor hydrothermal sulfide samples consist of major pyrite ± marcasite,  
176 chalcopyrite, sphalerite, anhydrite, barite, opal, and minor galena.



177 Sulfide, sulfate, and opal mineral aggregate samples were taken from various seafloor  
178 hydrothermal sulfide deposits. Samples denoted as pyrite, sphalerite, chalcopyrite +  
179 pyrite, sulfate, and opal consist of abundant (> 30%) pyrite ± marcasite, sphalerite,  
180 chalcopyrite + pyrite, anhydrite + barite, and opal respectively. All the samples were  
181 crushed and sieved to select sulfide, sulfate, and opal aggregates between >1 mm and  
182 1 cm. All mineral aggregate samples destined for noble gas analysis were then  
183 hand-picked carefully under a binocular microscope to avoid contamination by oxides.  
184 These samples were placed in distilled water, exposed to ultrasonic waves for 15 min,  
185 and washed in pure water (18.2 MΩ) to remove impurities from the surface. All  
186 samples were then dried and stored in a desiccator.

187 For noble gas analysis at GFZ Potsdam, samples of 0.13–1.1 g of various sulfide,  
188 sulfate, and opal mineral aggregates were loaded one at a time into an ultra-high  
189 vacuum crusher. For the first six samples analyzed (designated by \* in Tables 2 and 3),  
190 the crusher was baked at 100 °C for 24 h. However, a very slow reduction of pressure  
191 during pumping and baking as well as persisting high blanks after the baking  
192 procedure indicated that not only adsorbed atmospheric gases, but also part of the  
193 fluid inclusion-hosted original noble gases might be lost before crushing extraction.  
194 Therefore, for all remaining samples, the crusher was just pumped for typically 16–20  
195 h without baking before the blank measurement and subsequent crushing extraction.  
196 In the crusher used, gases are released from fluid inclusions by mechanically breaking  
197 the mineral grains between two hard metal jaws. The crushing efficiency (i.e., the  
198 amount of gas extracted compared to the total gas hosted in the fluid inclusions) is

199 estimated as between 50% and 100% for silicate minerals, but may be lower for some  
200 sulfides (cf. Jean-Baptiste and Fouquet, 1996; Lüders and Niedermann, 2010). Active  
201 gases were removed in two titanium sponge or foil getters and two SAES (ZrAl)  
202 getters before trapping the noble gases at 11 K on charcoal in a cryogenic adsorber.  
203 After sequential release, the noble gas concentrations and isotopic compositions were  
204 determined separately for helium, neon, argon, and krypton + xenon in a VG5400  
205 mass spectrometer. Static blanks (i.e., created without activating the crusher  
206 mechanism) measured before each sample gas extraction varied widely, depending  
207 mainly on the total gas content of the respective sample, from  $4\text{--}230 \times 10^{-12} \text{ cm}^3\text{STP}$   
208 (standard temperature and pressure)  $^4\text{He}$ ,  $1\text{--}1,200 \times 10^{-12} \text{ cm}^3 \text{STP}$   $^{20}\text{Ne}$ ,  $0.1\text{--}32 \times 10^{-8}$   
209  $\text{cm}^3 \text{STP}$   $^{40}\text{Ar}$ ,  $0.03\text{--}27 \times 10^{-12} \text{ cm}^3 \text{STP}$   $^{84}\text{Kr}$  and  $0.01\text{--}1.9 \times 10^{-12} \text{ cm}^3 \text{STP}$   $^{132}\text{Xe}$ .  
210 Even the highest blank values rarely exceeded 2%–3% of the total sample gas  
211 amounts, except for some Ne and Xe measurements.

212 The mass spectrometer sensitivity and the isotopic mass discrimination were  
213 determined using the GFZ laboratory standard provided by the Linde company, which  
214 is an artificial mixture of the five noble gases with an enhanced  $^3\text{He}/^4\text{He}$  ratio of  $15.58$   
215  $\pm 0.17 R_a$  and atmospheric isotopic compositions for neon, argon, krypton, and xenon.  
216 The calibration gas was originally cross-checked against glass ampoule gas standards  
217 provided by the University of Bern, and the  $^3\text{He}/^4\text{He}$  ratio was calibrated against air  
218 and the Japanese He standard (Matsuda et al., 2002). Details of the analytical  
219 procedures and data reduction methods used can be found in Niedermann et al.  
220 (1997).

221 All data have been corrected for analytical blanks, isobaric interferences ( $^{40}\text{Ar}^{++}$ ,  
222  $\text{CO}_2^{++}$ ,  $\text{H}^{35}\text{Cl}^+$ ,  $\text{H}^{37}\text{Cl}^+$ ), and mass discrimination effects. Error limits correspond to  
223 the 95% confidence level and include the statistical uncertainties of the measurement,  
224 the uncertainties of sensitivity and mass discrimination determinations, and the  
225 uncertainties of blank and interference corrections. Noble gas data were obtained for  
226 17 pyrite, 3 anhydrite+barite, 2 opal, 8 sphalerite, and 2 chalcopyrite+pyrite aggregate  
227 samples in total (Tables 2, 3). The reported concentrations of fluid inclusion-hosted  
228 noble gases in the sulfide, sulfate, and opal mineral samples are not concentrations in  
229 the fluid, but were determined per gram of solid sulfide, sulfate, and opal mineral  
230 crushed.

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### 243 **3. Results**

#### 244 *3.1. Helium*

245 The measured concentrations of fluid inclusion-hosted He in the investigated sulfide,  
246 sulfate, and opal mineral aggregate samples vary over three orders of magnitude ( $^4\text{He}$   
247  $0.0174\text{--}22.1 \times 10^{-8} \text{ cm}^3 \text{ STP/g}$ ) (Table 2, Fig. 2). Several pyrite aggregate samples  
248 from the EPR near  $13^\circ\text{N}$  have the highest  $^4\text{He}$  concentrations (up to  $22.1 \times 10^{-8} \text{ cm}^3$   
249  $\text{STP/g}$ , Table 2) of the entire sample suite, which are significantly higher than sulfide  
250 mineral samples from the EPR near  $1\text{--}2^\circ\text{S}$ , the MAR, the CIR, the SWIR, and the  
251 NFB (Table 2, Fig. 2). Furthermore, most of the  $^4\text{He}$  concentrations in sulfide mineral  
252 aggregate samples are significantly higher than those of sulfate mineral (anhydrite and  
253 barite) aggregates and opal mineral samples from the MAR and CIR (Table 2, Fig. 2).  
254 The  $^3\text{He}/^4\text{He}$  ratios in the sulfide aggregate samples vary from  $\sim 0.6$  to  $10.4 R_a$  (Table  
255 2, Fig. 3), and most of the  $^3\text{He}/^4\text{He}$  ratios of sulfide mineral samples are significantly  
256 less radiogenic than the modern atmosphere, lying within the MORB range or even  
257 somewhat higher (Figs. 3, 4). Only two samples possess  $^3\text{He}/^4\text{He}$  ratios ( $0.63^{+0.71}_{-0.64}$   
258  $R_a$ , S25-TVG21 from the SWIR near  $63.5^\circ\text{E}$ , and  $1.50 \pm 0.61 R_a$ , TVG13-9.1 from the  
259 EHF, CIR) that are within the error of the atmospheric value ( $1 R_a$ ; Figs. 3, 4).  
260 Although the fluid-inclusion population densities in these samples are not known, the  
261 variation in He concentrations may in part be due to differences in the fluid-inclusion  
262 population densities among the sulfide, sulfate, and opal samples, or to variations in  
263 crushing efficiency, which may also occur among different minerals (Jean-Baptiste  
264 and Fouquet, 1996). However, none of these parameters can probably explain the

265 observed three order of magnitude range in the present sample set. Furthermore, the  
266 helium concentrations in seafloor hydrothermal sulfide, sulfate, and opal mineral  
267 aggregate samples do not show any relationship with water depth or spreading rate.  
268 The pyrite mineral aggregates from the EPR near 13°N, from ~2500 m water depth on  
269 a ridge with moderately fast spreading velocity (~100 mm/yr), possess significantly  
270 higher He concentrations than the remaining samples from both shallower and deeper  
271 locations and from slower- and faster-spreading ridges (Tables 1, 2). The  $^3\text{He}/^4\text{He}$   
272 ratios show a slightly decreasing tendency with water depth; however, the significance  
273 of this trend is questionable because the data include different minerals and different  
274 settings (Tables 1, 2). There is clearly no trend in  $^3\text{He}/^4\text{He}$  ratios with spreading rate,  
275 which suggests that they are not controlled by this parameter.

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287 3.2. Neon, argon, krypton, and xenon

288 Neon, argon, krypton, and xenon concentrations are also variable and, like He, may be  
289 influenced to some extent by variations in fluid-inclusion population density or  
290 crushing efficiency. Sulfide, sulfate and opal mineral aggregates have  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$ ,  
291 and  $^{132}\text{Xe}$  concentrations from  $0.029\text{--}5.6 \times 10^{-8}$ ,  $28\text{--}3,500 \times 10^{-8}$ ,  $26\text{--}2,900 \times 10^{-12}$ , and  
292  $1.7\text{--}180 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$  (Tables 2, 3). The two sulfate mineral (anhydrite and barite)  
293 aggregates from the LHF on the MAR exhibit the highest Ne, Ar, and Kr  
294 concentrations ( $^{20}\text{Ne}$  3.88 and  $5.61 \times 10^{-8}$ ,  $^{40}\text{Ar}$  3060 and  $3480 \times 10^{-8}$ , and  $^{84}\text{Kr}$  2480  
295 and  $2850 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$ ), whereas one opal sample from the EHF shows the  
296 highest Xe concentration ( $^{132}\text{Xe}$   $184 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$ ) (Tables 2, 3). Generally, the  
297  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$ , and  $^{132}\text{Xe}$  concentrations in sulfate mineral aggregates and in opal  
298 samples from the LHF and EHF are significantly higher than those in sulfide mineral  
299 aggregate samples from the other study areas (Tables 2, 3). In addition, the Ne, Ar,  
300 and Xe isotopic ratios in the sulfide, sulfate and opal mineral aggregate samples have  
301 narrow ranges ( $^{20}\text{Ne}/^{22}\text{Ne}$  9.7–10.2;  $^{38}\text{Ar}/^{36}\text{Ar}$  0.1877–0.1912;  $^{129}\text{Xe}/^{132}\text{Xe}$   
302 0.979–0.993; see Tables 2, 3), showing no relationship with mineral aggregate type  
303 (Tables 2, 3).

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## 309 **4. Discussion**

### 310 *4.1. Noble gas sources*

#### 311 4.1.1 Helium sources

312 It is known that the  $^3\text{He}/^4\text{He}$  ratio of the MORB is  $\sim 8.5 R_a$  (e.g., Moreira et al., 1998;  
313 Graham, 2002). Modern OIB have much more variable  $^3\text{He}/^4\text{He}$  ratios that may reach  
314 values up to  $\sim 33 R_a$  (Honda et al., 1993). The  $^3\text{He}/^4\text{He}$  ratios of hydrothermal fluids  
315 from various hydrothermal fields all over the world's oceans range from  $\sim 5.7$  to  $10.0$   
316  $R_a$  (Jenkins et al., 1978; Lupton et al., 1980; Welhan and Craig, 1983; Kim et al., 1984;  
317 Merlivat et al., 1987; Jean-Baptiste et al., 1991, 1997, 1998, 2004; Rudnicki and  
318 Elderfield, 1992; Ishibashi et al., 1994, 1995; Charlou et al., 1996, 2000; Gamo et al.,  
319 2001; Keir et al., 2008) and are therefore close to the MORB range. Therefore, the  
320 helium isotopic compositions of seafloor sulfide deposits can be used as evidence for  
321 the source of helium (e.g., Stuart et al., 1994a).

322 The  $^3\text{He}/^4\text{He}$  ratios for the sulfide, sulfate, and opal mineral aggregate samples studied  
323 here fall into a broad range ( $\sim 0.6$ – $10.4 R_a$ ; Table 2, Fig. 3). A few samples from the  
324 NFB are characterized by a high  $^3\text{He}/^4\text{He}$  ratio  $>7 R_a$  (e.g., 113.1GTV:  $10.4 \pm 1.0 R_a$ ;  
325 Fig. 4). This value is almost indistinguishable from the  $^3\text{He}/^4\text{He}$  ratio of hydrothermal  
326 fluids currently venting from the NFB ( $9.04$ – $10.0 R_a$ ; Ishibashi et al., 1994),  
327 suggesting that the sulfide minerals from the NFB formed under high-temperature  
328 ( $>200^\circ\text{C}$ ) fluid conditions with only minor dilution by ambient seawater (Ishibashi et  
329 al., 1994). The absence of radiogenic He in fluid-inclusions from the sulfides formed  
330 by high-temperature mineralization suggests that the hydrothermal circulation

331 occurred within an active magmatic system and not within the underlying <1 Ma old  
332 oceanic crust (e.g., Malahoff et al., 1982; Auzende et al., 1988; Tanahashi et al., 1991;  
333 Huchon et al., 1994). Similarly, many samples from other settings have  $^3\text{He}/^4\text{He}$   
334 ratios  $> 7 R_a$ , i.e., within the range typical of the MORB-type isotope signatures found  
335 at their respective locations. Moreover, compared with atmospheric  $^3\text{He}/^{22}\text{Ne}$   
336 ( $4.36 \times 10^{-6}$ ) and  $^3\text{He}/^{36}\text{Ar}$  ratios ( $2.33 \times 10^{-7}$ ; Ozima and Podosek, 2002), the high  
337  $^3\text{He}/^{22}\text{Ne}$  ( $4.1\text{--}260 \times 10^{-5}$ ) and  $^3\text{He}/^{36}\text{Ar}$  ( $1.5\text{--}90 \times 10^{-6}$ ) ratios in such samples are  
338 consistent with the expected higher ratios in MOR magmas (MORB  $^3\text{He}/^{22}\text{Ne} = 5.1$ ,  
339  $^3\text{He}/^{36}\text{Ar} = 0.45$ ; Moreira et al, 1998; OIB  $^3\text{He}/^{22}\text{Ne} \approx 2.4$ ,  $^3\text{He}/^{36}\text{Ar} \approx 0.4$ ; Tieloff et  
340 al., 2000; Raquin and Moreira, 2009; Fűri et al., 2010), which also suggests that the  
341 He is derived from direct degassing of magmatic volatiles (e.g., Baker and Lupton,  
342 1990; Stuart et al., 1994b; Zeng et al., 2001). Likewise, the elemental abundance  
343 pattern (Fig. 5) shows that He/Ne and He/Ar ratios are one to three orders of  
344 magnitude higher than expected for air-saturated seawater in most sulfide samples.

345 Medium He isotopic ratio ( $1 R_a < ^3\text{He}/^4\text{He} < 7 R_a$ ) samples (Fig. 4) are abundant in the  
346 EHF, CIR. They have a broad range of  $^3\text{He}/^4\text{He}$  ratios between those of the MORB  
347 and the atmosphere (Table 2, Figs. 4 and 6) and He to heavier noble gas ratios similar  
348 to those of air or air-saturated seawater (Fig. 5). This suggests that these samples have  
349 likely been influenced by both radiogenic He from seawater and unradiogenic He  
350 released by the MORB mantle beneath the hydrothermal system. This pattern shows  
351 that the He in the medium He isotopic ratio samples is a mixture of seawater and  
352 MORB mantle He.



353 Two samples from the EHF and the A area (CIR and SWIR respectively) have low  
354  $^3\text{He}/^4\text{He}$  ratios ( $\sim 1 R_a$ ; Fig. 4) which are close to seawater and atmospheric values, and  
355 show air-like He to heavier noble gas ratios, indicating that their He is mainly derived  
356 from seawater (Fig. 6). Depressed  $^3\text{He}/^4\text{He}$  ratios (0.29–6.91  $R_a$ ) were also observed  
357 in fluid inclusions in pyrite and anhydrite from the PACMANUS hydrothermal field  
358 of Papua New Guinea and were interpreted as caused by significant atmospheric  
359 diffusive low-temperature fluid and seawater exchange (Webber et al., 2011).

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#### 375 4.1.2 Neon, argon, krypton, and xenon sources

376 Most of the Ne, Ar, and Xe isotopic ratios agree with values for the modern  
377 atmosphere (Ozima and Podosek, 2002; Lee et al., 2006) or are just slightly lower or  
378 higher (Tables 2, 3). Their values are significantly different from those of MORB and  
379 OIB mantle end-members, confirming that Ne, Ar, and Xe are derived mainly from  
380 ambient seawater (Fig. 6). This can be interpreted as evidence for entrainment of  
381 seawater into hydrothermal fluids (e.g., Stuart et al., 1994a).

382 Furthermore, the elemental abundance pattern of Ne, Ar, Kr, and Xe in fluid  
383 inclusions of sulfide, sulfate and opal samples is similar to that in air-saturated water  
384 (Fig. 5), which also suggests that the heavier noble gases in all the sulfide, sulfate, and  
385 opal samples are predominantly derived from ambient seawater. Kr isotopic ratios  
386 were not measured because they do not vary among different terrestrial reservoirs and  
387 are therefore not indicative of the fluid source. Consequently, it was not possible to  
388 assess the source of Kr in sulfide, sulfate, and opal mineral aggregate samples based  
389 on Kr isotope data. However, the elemental abundance pattern (Fig. 5) and the  
390 observation that Kr concentrations in the present samples show positive correlations  
391 with Ne and Ar concentrations indicate that Kr, like Ne and Ar, is derived mainly from  
392 seawater.

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397 4.2. Noble gas enrichment

398 The high concentrations of He in the present seafloor sulfide samples are consistent  
399 with those in seafloor sulfides from other studies (Turner and Stuart, 1992; Stuart et  
400 al., 1994a, 1994b, 1995; Jean-Baptiste and Fouquet, 1996; Zeng et al., 2001, 2004;  
401 Lüders and Niedermann, 2010; Webber et al., 2011), which suggests that they are due  
402 to extraction of mantle volatiles from magma by circulating hydrothermal fluids (e.g.,  
403 Baker and Lupton, 1990). In addition, most of the helium concentrations of the sulfide  
404 aggregate samples are significantly higher than those in opal minerals, which form  
405 under low-temperature (< 200°C) conditions (e.g., Fouquet et al., 1988; Dekov et al.,  
406 2013) and are known to leak helium (e.g., Trull et al., 1991). The  $^4\text{He}$  concentration in  
407 hydrothermal fluids ( $10^{-6}$  to  $10^{-5}$  cm<sup>3</sup>STP/g; Fourre et al., 2006) is significantly higher  
408 than that in seawater ( $\sim 3.8 \times 10^{-8}$  cm<sup>3</sup>STP/g). However, due to its low concentration,  
409 the helium in opal minerals is much more susceptible to dilution with ambient  
410 seawater (Jean-Baptiste and Fouquet, 1996), and loss of He at low temperatures acts  
411 against preservation of the initial hydrothermal fluid  $^3\text{He}/^4\text{He}$  ratios in opal minerals.

412 In principle, low He concentrations and/or low  $^3\text{He}/^4\text{He}$  ratios in sulfate, opal and  
413 several sulfide (e.g., sample S25-TVG21) aggregate samples might also indicate a  
414 contribution of radiogenic helium produced by in-situ decay of U and Th. The typical  
415 U-Th content of hydrothermal sulfate, opal and sulfide samples on the EPR is in the  
416 range of 1–10 ppm U and 0.1–1 ppm Th (Lalou and Brichet, 1982, 1987). However,  
417 the ages of sulfate, opal, and sulfide deposits sampled from the EPR are very young,  
418 ranging from 0 to 20 years in most cases (Lalou et al., 1985), which rules out any

419 significant radiogenic He production. Furthermore, based on the diffusion coefficient  
420 of He in sulfides, a simple diffusion calculation shows that the  $^3\text{He}/^4\text{He}$  ratios cannot  
421 be decreased from MORB-like to much lower values by fractionation in seafloor  
422 sulfide deposits over the typical ages of these sulfide deposits (Jean-Baptiste and  
423 Fouquet, 1996). Hence, the lower He concentrations and/or  $^3\text{He}/^4\text{He}$  ratios in sulfate,  
424 opal, and several sulfide aggregate samples are most likely related to mixing of the  
425 end-member hydrothermal fluid with ambient seawater. For the sulfate and opal  
426 samples, significant seawater He contribution is also evident in the elemental  
427 abundance pattern (Fig. 5).

428 Within individual seafloor hydrothermal systems, He concentrations vary on short  
429 time scales in response to magmatic-tectonic processes (Baker and Lupton, 1990) or  
430 to changes in hydrothermal system plumbing (Butterfield et al., 1990). Despite this,  
431 vent-fluid  $^3\text{He}/^4\text{He}$  ratios remain constant (Lupton et al., 1989). The results presented  
432 here imply that when using sulfides to reconstruct the characteristics of hydrothermal  
433 fluids, care must be taken to select high-temperature sulfide minerals by mineralogical  
434 analyses (Jean-Baptiste and Fouquet, 1996) due to He depletion in low-temperature  
435 sulfide, sulfate, and opal minerals. In addition, sulfide minerals, because of their low  
436 ionic porosity and low U and Th contents ( $^{238}\text{U} < 10$  ppm,  $^{232}\text{Th} < 1$  ppm; Lalou et al.,  
437 1993, 1996; You and Bickle, 1998; Münch et al., 2001), preserve the He isotope ratios  
438 of the initial fluid considerably better than sulfate and silicate minerals.

439 The Ne, Ar, Kr, and Xe concentrations in sulfate and opal mineral samples are  
440 significantly higher than in sulfide aggregate samples. Barite and opal minerals from

441 the EPR near 13°N and the Panarea Platform of the Aeolian Arc in the Tyrrhenian Sea  
442 were all formed under low-temperature (< 200°C) conditions (e.g., Fouquet et al.,  
443 1988; Dekov et al., 2013), suggesting that low-temperature sulfide minerals (e.g.,  
444 pyrite and sphalerite), sulfate mineral aggregates, and opal samples can trap high  
445 concentrations of Ne, Ar, Kr and Xe, as well as hydrated phyllosilicates (chlorite,  
446 serpentine, and talc; Podosek et al., 1980) as a result of low-temperature fluid  
447 interaction and/or gas adsorption. This intuitively suggests that Ne, Ar, Kr, and Xe are  
448 enriched under low temperature (< 200°C) conditions.

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463 4.3. Helium and heat fluxes

464 In general, the sulfide, sulfate, and opal mineral aggregate samples yielded 0.12–22×  
 465  $10^{-8}$  cm<sup>3</sup> STP <sup>4</sup>He/g, 0.16–0.72×  $10^{-8}$  cm<sup>3</sup> STP <sup>4</sup>He/g, and 0.017–0.028 ×  $10^{-8}$  cm<sup>3</sup> STP  
 466 <sup>4</sup>He/g respectively. In comparison, high-temperature (>300 °C) vent fluid He  
 467 concentrations have been found to range from 0.09 to  $6.0 \times 10^{-5}$  cm<sup>3</sup> STP <sup>4</sup>He/g fluid  
 468 (e.g., Merlivat et al., 1987; Jean-Baptiste et al., 1991, 1997; Rudnicki and Elderfield,  
 469 1992; Ishibashi et al., 1994), suggesting that the mineral aggregates have trapped  
 470 roughly  $0.2\text{--}2400 \times 10^{-4}$  g hydrothermal fluid / g sulfide,  $0.2\text{--}80 \times 10^{-4}$  g  
 471 hydrothermal fluid / g sulfate, and  $0.03\text{--}3 \times 10^{-4}$  g hydrothermal fluid / g opal. This  
 472 implies in turn that the sulfide mineral aggregate samples have trapped more  
 473 hydrothermal fluids (up to 24%) than the sulfate (up to 0.8%) and opal (less than 0.1%)  
 474 mineral samples in modern seafloor hydrothermal sulfide deposits.

475 Furthermore, if the deposition temperature of the minerals containing the fluids can be  
 476 established, assuming that all the Ne comes from seawater and that the <sup>20</sup>Ne/<sup>22</sup>Ne and  
 477 <sup>3</sup>He/<sup>4</sup>He ratios in seawater are equal to the atmospheric values, a combination of the  
 478 temperature and isotopic ratios of MORB mantle helium and neon can be used to  
 479 estimate helium/heat ratios, He/Q. The following equations apply:

$$480 \quad {}^3\text{He}/\text{Q} = ({}^3\text{He}/{}^{22}\text{Ne})_{\text{m}} \times (({}^4\text{He}/{}^3\text{He})_{\text{m}} - ({}^4\text{He}/{}^3\text{He})_{\text{a}}) / (({}^4\text{He}/{}^3\text{He})_{\text{b}} - ({}^4\text{He}/{}^3\text{He})_{\text{a}}) \times ({}^{22}\text{Ne})_{\text{s}} /$$

$$481 \quad (C_p \times T) \quad (1)$$

$$482 \quad {}^4\text{He}/\text{Q} = ({}^4\text{He}/{}^{20}\text{Ne})_{\text{m}} \times (({}^{20}\text{Ne}/{}^4\text{He})_{\text{m}} - ({}^{20}\text{Ne}/{}^4\text{He})_{\text{s}}) / (({}^{20}\text{Ne}/{}^4\text{He})_{\text{b}} - ({}^{20}\text{Ne}/{}^4\text{He})_{\text{s}}) \times$$

$$483 \quad ({}^{20}\text{Ne})_{\text{s}} / (C_p \times T) \quad (2)$$

484 where (<sup>22</sup>Ne)<sub>s</sub> and (<sup>20</sup>Ne)<sub>s</sub> are the concentrations of <sup>22</sup>Ne ( $1.71 \times 10^{-8}$  cm<sup>3</sup> STP/g) and

485  $^{20}\text{Ne}$  ( $1.68 \times 10^{-7} \text{ cm}^3 \text{ STP/g}$ ) in seawater,  $C_p$  is the heat capacity of seawater ( $5.8 \text{ J K}^{-1}$   
486  $\text{g}^{-1}$ ; Elderfield and Schultz, 1996), and  $T$  is the temperature difference between vent  
487 fluid and seawater, which is essentially equal to the vent-fluid temperature in  $^\circ\text{C}$ . The  
488 subscripts m, b, a, and s refer to the sample, the MORB mantle, the atmosphere, and  
489 seawater respectively.

490 Assuming a vent fluid temperature of  $350 \text{ }^\circ\text{C}$ , Eqs. (1) and (2) were applied to the  
491 sulfide mineral aggregate samples to calculate  $^3\text{He}/\text{Q}$  ( $0.22\text{--}3.44$ , avg  $1.09 \times 10^{-14} \text{ cm}^3$   
492  $\text{STP/J}$ ) and  $^4\text{He}/\text{Q}$  ( $0.17\text{--}3.13$ , avg  $0.97 \times 10^{-9} \text{ cm}^3 \text{ STP/J}$ ), which are extracted  
493 through hydrothermal activity from the MORB and/or the OIB mantle. The He/heat  
494 ratios in the MORs (EPR near  $13^\circ\text{N}$ , EPR near  $1\text{--}2^\circ\text{S}$ , KHF and EHF in the CIR:  
495  $^3\text{He}/\text{Q} = 0.36\text{--}3.44 \times 10^{-14} \text{ cm}^3 \text{ STP/J}$ ;  $^4\text{He}/\text{Q} = 0.32\text{--}3.13 \times 10^{-9} \text{ cm}^3 \text{ STP/J}$ ) are not  
496 significantly different from those in the back-arc NFB ( $^3\text{He}/\text{Q} = 0.22\text{--}1.97 \times 10^{-14} \text{ cm}^3$   
497  $\text{STP/J}$ ;  $^4\text{He}/\text{Q} = 0.17\text{--}1.50 \times 10^{-9} \text{ cm}^3 \text{ STP/J}$ ). However, these values are an order of  
498 magnitude lower than those ( $^3\text{He}/\text{Q} 1.5 \times 10^{-13} \text{ cm}^3 \text{ STP/J}$ ;  $^4\text{He}/\text{Q} 1.4 \times 10^{-8} \text{ cm}^3 \text{ STP/J}$ )  
499 calculated by Turner and Stuart (1992) using the concentrations of  $^{36}\text{Ar}$  ( $1.26 \times 10^{-6}$   
500  $\text{cm}^3 \text{ STP/g}$ ) and  $^{40}\text{Ar}$  ( $3.73 \times 10^{-4} \text{ cm}^3 \text{ STP/g}$ ) in Pacific deep water (Bieri and Koide,  
501 1972).

502 The mass of high-temperature ( $350 \text{ }^\circ\text{C}$ ) hydrothermal fluid emanating from mid-ocean  
503 ridges is on the order of  $0.3\text{--}0.6 \times 10^{13} \text{ kg/yr}$  (Elderfield and Schultz, 1996). Assuming  
504 helium concentrations of  $0.09$  to  $6.0 \times 10^{-5} \text{ cm}^3 \text{ STP } ^4\text{He/g}$  fluid in high-temperature  
505 ( $> 300 \text{ }^\circ\text{C}$ ) vent fluids (Merlivat et al., 1987; Jean-Baptiste et al., 1991, 1997;  
506 Rudnicki and Elderfield, 1992; Ishibashi et al., 1994, 1995) and using  $^4\text{He}/\text{Q}$  of  $0.97 \times$

507  $10^{-9}$  cm<sup>3</sup> STP/J, global helium and heat fluxes to high-temperature hydrothermal vents  
508 are approximately  $0.05\text{--}6 \times 10^4$  kg per year of helium, and  $0.1\text{--}12 \times 10^{12}$  W of heat,  
509 which cover the range ( $1.1\text{--}6.2 \times 10^{12}$  W) of vent heat flux estimated by Elderfield and  
510 Schultz (1996). Using a total oceanic heat flux of  $32 \times 10^{12}$  W (Elderfield and Schultz,  
511 1996), this suggests that roughly 0.3% or more of ocean heat is supplied by seafloor  
512 high-temperature hydrothermal activity. In addition, the amount of seafloor massive  
513 sulfide deposits in the global oceans has been estimated as on the order of  $6 \times 10^8$   
514 tonnes (Hannington et al., 2011) using new deposit occurrence data from 10,000 km  
515 of ridge, arc, and back-arc spreading centers. Approximately 65% and 22% of global  
516 seafloor hydrothermal sulfide deposits occur along MORs and BABs (Hannington et  
517 al., 2011) respectively, suggesting that helium and heat fluxes to high-temperature  
518 hydrothermal vents are approximately  $0.03\text{--}3.9 \times 10^4$  kg per year and  $0.07\text{--}7.8 \times 10^{12}$   
519 W in MORs, or  $0.01\text{--}1.3 \times 10^4$  kg per year and  $0.02\text{--}2.6 \times 10^{12}$  W in BABs.

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791

792

793 **Figure Captions**

794 **Fig. 1.** Locations of seafloor hydrothermal sulfide samples from the deep-sea  
795 hydrothermal fields analyzed for noble gas concentrations and isotopic compositions  
796 in this study: KHF–Kairei hydrothermal field; EHF–Edmond hydrothermal field;  
797 CIR–Central Indian Ridge; SWIR–Southwest Indian Ridge; S99HF–Sonne 99  
798 hydrothermal field; NFB–North Fiji Basin; EPR–East Pacific Rise; LHF–Logatchev  
799 hydrothermal field; MAR–Mid-Atlantic Ridge.

800

801 **Fig. 2.** Concentrations of  $^4\text{He}$  in seafloor hydrothermal sulfide, sulfate and opal  
802 mineral aggregate samples: Q–opal; Anh–anhydrite; Ba–barite; Sph–sphalerite;  
803 Py–pyrite; Cpy–chalcopyrite.

804

805 **Fig. 3.**  $^3\text{He}/^4\text{He}$  ratios of seafloor hydrothermal sulfide, sulfate (LHF, EHF) and opal  
806 (EHF, CIR) samples from this study and the literature.  $R_a$  is the atmospheric  $^3\text{He}/^4\text{He}$   
807 ratio ( $1.4 \times 10^{-6}$ ). Colored symbols represent results obtained in this work, gray shading  
808 results from the literature. Literature data are from EPR 13°N, Stuart et al. (1995) and  
809 Jean-Baptiste and Fouquet (1996); EPR 21°N, Turner and Stuart (1992) and Stuart et  
810 al. (1994b); Middle Valley, Stuart et al. (1994a, b); TAG, Stuart et al. (1994b) and  
811 Zeng et al. (2001); Snake Pit, Stuart et al. (1994b); JADE, Zeng et al. (2004), Hou et  
812 al. (2005), and Lüders and Niedermann (2010); PACMANUS, Webber et al. (2011);  
813 NFB, Lüders and Niedermann (2010).

814

815 **Fig. 4.**  $^3\text{He}/^4\text{He}$  ratios of different mineral aggregates from seafloor hydrothermal  
816 sulfide deposits. Atmospheric, MORB mantle, and OIB mantle data are from Ozima  
817 and Podosek (2002) and Graham (2002).  $2\sigma$  error limits are shown.

818

819 **Fig. 5.** Elemental abundance patterns (relative to atmospheric abundance and  $^{40}\text{Ar}$ ) of  
820 noble gases in seafloor hydrothermal sulfide, sulfate and opal mineral aggregates. The  
821 fractionation factor is defined as  $(^i\text{X}/^{40}\text{Ar})_{\text{sample}}/(^i\text{X}/^{40}\text{Ar})_{\text{air}}$ , where  $^i\text{X}$  is a noble gas  
822 isotope. Fractionation patterns for dissolution equilibrium of noble gases in seawater  
823 are given for 0 °C, 25 °C, and 50 °C according to Smith and Kennedy (1983) and for  
824 100 °C according to Crovetto et al. (1982).

825

826 **Fig. 6.** (a)  $^{20}\text{Ne}/^{22}\text{Ne} - ^3\text{He}/^4\text{He}$  systematics, and (b)  $^{40}\text{Ar}/^{36}\text{Ar} - ^3\text{He}/^4\text{He}$  systematics  
827 of fluid inclusions in seafloor hydrothermal sulfide, sulfate and opal mineral  
828 aggregates, compared with literature data for various mantle-derived samples (gray  
829 symbols). The plot was drawn according to the method outlined by Langmuir et al.  
830 (1978): Mixing line 1 is between the MORB mantle and the atmosphere endmember  
831 components; mixing line 2 is between the OIB mantle and the atmosphere  
832 end-member components. Atmospheric, MORB mantle, and OIB mantle data are from  
833 Ozima and Podosek (2002), Graham (2002), and Lee et al. (2006). MORB values are  
834 from Ozima and Zashu (1983), Hiyagon et al. (1992), and Niedermann et al. (1997).  
835 OIB samples are from Hiyagon et al. (1992), Honda et al. (1993), and Valbracht et al.  
836 (1997).

837

838 **Table 1** Description of seafloor hydrothermal sulfide samples analyzed for noble gas  
839 concentrations and isotopic compositions in this study.

840

841 **Table 2** Concentrations and isotopic compositions of fluid inclusion-hosted He, Ne,  
842 and Ar in seafloor hydrothermal sulfide, sulfate and opal mineral aggregate samples  
843 from the EPR near 13°N and 1-2°S, LHF, MAR near 13°S, KHF, EHF, A area, SWIR  
844 near 63.5°E, and S99HF. Gas concentrations are in units of  $10^{-8}$  cm<sup>3</sup> STP/g of mineral.  
845 They depend on crushing efficiency, which is estimated to be between 50% and 100%,  
846 and may in some cases have been reduced by partial gas loss in the vacuum line  
847 before sample crushing (see text). Error limits are  $2\sigma$ .

848

849 **Table 3** Concentrations and isotopic compositions of fluid inclusion-hosted Kr and Xe  
850 in seafloor hydrothermal sulfide, sulfate and opal mineral aggregate samples.

851

**Table 1** Description of seafloor hydrothermal sulfide samples analyzed for noble gas concentrations and isotopic compositions in [this](#) study.

Field	Sample	Latitude	Longitude	Depth (m)	Description	Sulfide mineralogy
<i>Fast-spreading mid-ocean ridge</i>						
13°N, EPR	TVG1-2	12°42.669'N	103°54.426'W	2,628	Fe-rich massive sulfides coated with tan Fe hydroxides, and small conduits	Py +++; Sp +, Cpy +
13°N, EPR	TVG1-3	12°42.669'N	103°54.426'W	2,628	Fe-rich massive sulfides coated with tan Fe hydroxides, and oxidized pyrite aggregates	Py +++; Cpy +, Sp +
13°N, EPR	TVG2-1	12°42.678'N	103°54.414'W	2,633	Fe-rich massive sulfides coated with tan Fe hydroxides and many elliptical cavities, showing development of mineral zoning	Py +++; Mc +++; Sp +
<i>Ultra-fast spreading mid-ocean ridge</i>						
1-2°S, EPR	S4-TVG1-1	1°22.130'S	102°37.360'W	2,747	Porous chimney fragment coated with tan Fe hydroxides and partially filled conduits	Py +++; Mc +, Cpy +; Sp +
1-2°S, EPR	S4-TVG1-2	1°22.130'S	102°37.360'W	2,747	Chimney fragment coated with tan Fe hydroxides	Py +++; Cpy ++, Mc ++; Sp +
1-2°S, EPR	S6-TVG3	2°09.102'S	102°38.760'W	2,921	Outer chimney wall fragment coated with red brown Fe hydroxides and white anhydrite layer	Mc +++; Py +++; Sp ++; Cpy +
<i>Slow-spreading mid-ocean ridge</i>						
LHF, MAR	TVG1-10	14°45.186'N	44°58.772'W	3,025	Fragment with anhydrite, barite, amorphous silica, disseminated pyrite, marcasite and chalcopyrite	Anh+++; Ba+++; Cpy ++, Py ++, Mc++
13°S, MAR	S7-TVG4-2	13°17.203'S	14°24.837'W	2,311	Zn-Fe rich massive sulfide fragment coated with Fe hydroxides and Cu sulfides	Sp+++; Py+++; Cpy+
<i>Intermediate-spreading mid-ocean ridge</i>						
KHF, CIR	TVG9	25°19.221'S	70°02.420'E	2,437	Chimney fragment with finely bladed chalcopyrite	Py +++; Cpy +



EHF, CIR	TVG12	23°52.678'S	69°35.808'E	3,293	Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, amorphous silica, nodular structure in the outside	Sp+++; Q+++; Py++, Mc++; Cpy+
EHF, CIR	TVG13-9.1	23°52.684'S	69°35.795'E	3,292	Irregular crust consisted of red brown to yellowish green oxide, anhydrite and gypsum, barite, with disseminated sulfides	Anh+++; Py+++; Mc+++; Cpy++, Sp++, Gyp++; Ba+
EHF, CIR	TVG13-9.2	23°52.684'S	69°35.795'E	3,292	Chimney fragment with red, brown and yellowish green mixture of oxide, anhydrite and gypsum	Mc+++; Anh+++; Gyp++, Cpy++, Sp++, Py++; Ba+
EHF, CIR	S18-TVG9	23°52.638'S	69°35.850'E	3,282	Porous Fe-Cu rich sulfides with minor sulfates	Py+++; Mc++, Sp++, Cpy++; Ba+
<i>Ultra-slow spreading mid-ocean ridge</i>						
A area, SWIR	21VII-TVG22	37°56.316'S	49°15.894'E	1,443	Fe-rich chimney fragment coated with grey amorphous silica, conduits partially in-filled with oxides	Cpy+++; Py+++; Mc++, Sp+
63.5°E, SWIR	S25-TVG21	27°57.042'S	63°32.484'E	3,666	Fe-rich massive sulfide fragment coated with Fe hydroxides and Cu sulfide	Mc+++; Py++; Cpy++
<i>Back-arc basin</i>						
S99HF, NFB	26.1GTV	16°57.602'S	173°54.991'E	1,976	Inner Zn-rich chimney wall fragment with yellowish brown oxides	Sp+++; Mc+, Cpy+
S99HF, NFB	26.2GTV	16°57.602'S	173°54.991'E	1,976	Grey Zn-rich chimney fragment with local honeycomb structure and coarse black sphalerite crystals	Sp+++; Mc+, Cpy+
S99HF, NFB	42GTV	16°57.533'S	173°54.978'E	1,975	Cu-rich chimney fragment with conduits	Cpy+++; Py++, Mc++
S99HF, NFB	113.1GTV	16°57.322'S	173°54.970'E	1,967	Porous massive sulfide	Py+++; Cpy++, Mc++
S99HF, NFB	113.2GTV	16°57.322'S	173°54.970'E	1,967	Porous Fe-rich massive sulfide	Py+++; Mc++, Sp++, Cpy++

Py-pyrite; Mc-marcasite; Cpy-chalcopyrite; Sp-sphalerite; Anh-anhydrite; Gyp-gypsum; Ba-barite; Q-opal. +++: abundant (>30%); ++: major (5-30%); +: minor (≤5%).

**Table 2** Concentrations and isotopic compositions of fluid inclusion-hosted He, Ne, and Ar in seafloor hydrothermal sulfide, sulfate and opal mineral aggregate samples from the EPR near 13°N and 1-2°S, LHF, MAR near 13°S, KHF, EHF, A area, SWIR near 63.5°E, and S99HF. Gas concentrations are in units of 10<sup>-8</sup> cm<sup>3</sup> STP/g of mineral. They depend on crushing efficiency, which is estimated to be between 50% and 100%, and may in some cases have been reduced by partial gas loss in the vacuum line **before** sample crushing (see text). Error limits are 2σ.

Sample	Mineral, Weight (g)	Analysis #	<sup>4</sup> He	<sup>20</sup> Ne	<sup>40</sup> Ar	<sup>3</sup> He/ <sup>4</sup> He (R <sub>a</sub> )	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>21</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>38</sup> Ar/ <sup>36</sup> Ar
<i>East Pacific Rise near 13°N</i>										
TVG1-2 (I)	Py, 0.60128	C190	16.41±0.82	1.179±0.071	355±21	7.79±0.24	-	-	299.9±3.0	-
TVG1-2 (II)	Py, 0.12892	C197	22.1±1.1	0.581±0.035	357±13	7.94±0.46	9.820±0.059	0.02928±0.00065	300.06±0.95	0.18825±0.00073
TVG1-3	Py, 0.62956	C191	7.40±0.37	0.840±0.051	332±21	7.72±0.44	-	-	299.9±2.4	0.1890±0.0013
TVG2-1-1	Py, 0.44600	C192	17.62±0.88	0.502±0.030	237±14	7.76±0.26	9.806±0.033	0.02952±0.00043	300.9±2.2	0.1877±0.0011
TVG2-1-2	Py, 0.46346	C193	11.71±0.59	1.153±0.069	538±32	7.72±0.24	9.777±0.034	0.02937±0.00036	298.5±1.1	0.18800±0.00097
<i>East Pacific Rise near 1-2°S</i>										
S4-TVG1-1 (I)*	Py, 0.78554	C170	0.765±0.038	0.0321±0.0021	28.4±4.6	8.1±0.71	9.748±0.048	0.02930±0.00094	298.4±1.4	0.1886±0.0010
S4-TVG1-1 (II)	Py, 0.56780	C179	2.21±0.11	0.278±0.016	158±11	7.9±0.7	9.853±0.077	0.02896±0.00036	295.8±1.5	0.1884±0.0011
S4-TVG1-2*	Py, 1.10150	C171	0.542±0.027	0.1125±0.0074	114±10	8.2±0.9	9.820±0.034	0.02889±0.00041	297.0±2.3	0.1885±0.0011
S6-TVG3*	Py, 0.88200	C172	4.18±0.21	0.794±0.036	511±70	8.22±0.44	9.824±0.024	0.02873±0.00021	295.6±2.1	0.1883±0.0010
<i>Logatchev hydrothermal field, Mid-Atlantic Ridge</i>										
TVG1-10-2	Anh+Ba, 0.60296	C201	0.1634±0.0085	3.88±0.21	3060±220	7.8±1.8	9.736±0.035	0.02877±0.00031	299.8±1.4	0.1884±0.0010
TVG1-10-1	Anh+Ba, 0.50910	C202	0.229±0.012	5.61±0.29	3480±250	7.4±0.9	9.794±0.043	0.02911±0.00028	299.0±1.2	0.1884±0.0011
<i>Mid-Atlantic Ridge near 13°S</i>										

S7-TVG4-2	Py, 0.59680	C189	0.327±0.016	0.213±0.017	169±10	7.1±1.8	-	-	298.7±1.8	0.1883±0.0011
<i>Kairei hydrothermal field, Central Indian Ridge</i>										
TVG9-1*	Py, 0.57712	C173	4.80±0.24	0.531±0.036	308±27	7.68±0.27	9.856±0.027	0.02887±0.00033	297.5±1.6	0.18826±0.00095
TVG9-2*	Py, 0.57524	C174	5.05±0.25	1.033±0.045	518±45	7.52±0.49	9.866±0.022	0.02882±0.00023	297.5±1.2	0.18832±0.00095
<i>Edmond hydrothermal field, Central Indian Ridge</i>										
TVG12-4 (I)*	Opal, 0.79852	C175	0.0174±0.0011	2.23±0.14	1140±150	4.9±2.2	-	-	294.2±2.4	0.1887±0.0010
TVG12-4 (II)	Opal, 0.25438	C176	0.0283±0.0023	3.83±0.23	1380±160	8.1±5.8	-	-	296.7±1.7	0.1884±0.0011
TVG12-5	Sph, 0.65574	K235	0.732±0.044	3.25±0.17	1620±170	7.04±0.51	9.855±0.043	0.02835±0.00034	299.3±1.3	0.1898±0.0013
TVG12-8	Sph, 0.66556	K232	0.1523±0.0077	0.1082±0.0057	200±14	7.6±1.4	9.844±0.056	0.02877±0.00047	300.1±1.3	0.1880±0.0011
TVG12-9	Sph, 0.65748	K233	0.206±0.010	0.343±0.018	383±26	5.0±1.8	9.831±0.037	0.02917±0.00043	300.6±1.3	0.1912±0.0011
TVG12-11	Sph, 0.64258	K234	0.305±0.018	0.199±0.010	231±16	5.5±1.2	10.200±0.044	0.02942±0.00049	295.8±1.3	0.1870±0.0012
TVG12-14	Sph, 0.66484	K236	0.621±0.037	0.0741±0.0041	202±14	7.9±1.0	9.816±0.073	0.02897±0.00069	299.9±1.1	0.1891±0.0010
TVG13-9.1	Anh/Ba, 0.60492	K239	0.719±0.036	1.562±0.094	888±98	1.50±0.61	9.939±0.054	0.02878±0.00038	298.4±1.6	0.1879±0.0016
TVG13-9.2	Py, 0.57428	C177	2.36±0.12	0.565±0.033	375±26	7.58±0.39	9.808±0.025	0.02901±0.00038	296.4±1.4	0.18818±0.00097
S18-TVG9	Py, 0.57318	C178	3.20±0.16	0.686±0.040	424±29	7.22±0.40	9.841±0.025	0.02902±0.00033	297.2±1.3	0.18815±0.00092
<i>A area, Southwest Indian Ridge</i>										
TVG22	Py, 0.60364	K237	0.1218±0.0086	0.1355±0.0077	265±18	8.5±1.9	9.797±0.068	0.02900±0.00082	301.4±1.2	0.1894±0.0011
<i>Southwest Indian Ridge near 63.5°E</i>										
S25-TVG21	Py, 0.59026	K238	0.869±0.066	2.11±0.22	1340±130	0.63 <sup>+0.71</sup> <sub>-0.63</sub>	9.892±0.055	0.02937±0.00048	299.2±1.2	0.1909±0.0013
<i>Sonne 99 hydrothermal field, North Fiji Basin, Back-arc Basin</i>										
26.1GTV-1	Sph, 0.60020	C195	0.536±0.027	0.0291±0.0019	33.5±1.5	9.4±1.1	-	-	298.8±1.3	0.18816±0.00089
26.1GTV-2	Sph, 0.61818	C196	0.1731±0.0088	0.0564±0.0042	192±12	9.8±4.5	-	-	297.6±1.5	0.1888±0.0012
26.2GTV	Sph, 0.70824	C198	0.215±0.011	0.245±0.017	337±18	9.0±1.0	-	-	297.4±1.4	0.1884±0.0011
42GTV	Cpy+Py, 0.61930	C199	0.192±0.010	0.307±0.019	183.9±9.6	8.1±2.2	-	-	295.9±2.5	0.1890±0.0017
113.1GTV	Cpy+Py, 0.60398	C200	0.275±0.014	0.469±0.030	794±41	10.4±1.0	-	-	296.5±1.4	0.1890±0.0011

113.2GTV	Py, 0.64228	C194	1.099±0.055	0.485±0.029	999±81	8.71±0.55	9.752±0.054	0.02941±0.00044	296.2 ±1.8	0.1882±0.0013
Atmosphere						1	9.80	0.0290	298.56	0.1885

“-” Indicates no data available due to experimental problems, notably high background of chemically active gases.  $(^3\text{He}/^4\text{He})_a = 1.39 \times 10^{-6}$ . Atmosphere data from Ozima and Podosek (2002) for He and Ne and from Lee et al. (2006) for Ar, respectively. Samples denoted by \* were baked for 24 hours at 100 °C before crushing extraction.

**Table 3** Concentrations and isotopic compositions of fluid inclusion-hosted Kr and Xe in seafloor hydrothermal sulfide, sulfate and opal mineral aggregate samples.

Sample	Mineral, Weight (g)	Analysis #	$^{84}\text{Kr}$ 10 <sup>-12</sup>	$^{132}\text{Xe}$ 10 <sup>-12</sup>	$^{128}\text{Xe}/^{132}\text{Xe}$	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{130}\text{Xe}/^{132}\text{Xe}$	$^{131}\text{Xe}/^{132}\text{Xe}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
<i>East Pacific Rise near 13°N</i>										
TVG1-2 (I)	Py, 0.60128	C190	261±16	65.6±5.6	0.0709±0.0011	0.984±0.010	0.1516±0.0013	0.7896±0.0072	0.3868±0.0034	0.3278±0.0040
TVG1-2 (II)	Py, 0.12892	C197	317±14	17.6±1.1	0.0723±0.0018	0.988±0.017	0.1532±0.0061	0.797±0.016	0.391±0.012	0.3302±0.0071
TVG1-3	Py, 0.62956	C191	252±16	27.2±2.3	0.0715±0.0010	0.9871±0.0088	0.1518±0.0016	0.7900±0.0057	0.3882±0.0036	0.3294±0.0038
TVG2-1-1	Py, 0.44600	C192	198±12	12.4±1.6	0.0718±0.0022	0.983±0.016	0.1513±0.0026	0.790±0.010	0.3872±0.0066	0.3278±0.0062
TVG2-1-2	Py, 0.46346	C193	415±25	18.5 <sup>+2.7</sup> <sub>-1.8</sub>	0.0714±0.0013	0.9873±0.0090	0.1516±0.0027	0.790±0.011	0.3886±0.0045	0.3297±0.0060
<i>East Pacific Rise near 1-2°S</i>										
S4-TVG1-1 (I)*	Py, 0.78554	C170	25.5±2.1	1.73±0.12	0.0703±0.0053	0.980±0.025	0.1524±0.0093	0.800±0.019	0.387±0.010	0.329±0.013
S4-TVG1-1 (II)	Py, 0.56780	C179	149±11	10.93 <sup>+0.90</sup> <sub>-0.80</sub>	0.0728±0.0022	0.983±0.011	0.1510±0.0028	0.7855±0.0092	0.3865±0.0049	0.3272±0.0040
S4-TVG1-2*	Py, 1.10150	C171	82.0±6.2	4.49 <sup>+0.39</sup> <sub>-0.23</sub>	0.0719±0.0016	0.979±0.012	0.1516±0.0026	0.785±0.011	0.3849±0.0071	0.3273±0.0059
S6-TVG3*	Py, 0.88200	C172	418±46	20.7±1.1	0.0724±0.0015	0.9825±0.0078	0.1520±0.0021	0.7891±0.0049	0.3871±0.0036	0.3284±0.0032
<i>Logatchev hydrothermal field, Mid-Atlantic Ridge</i>										
TVG1-10-2	Anh+Ba, 0.60296	C201	2480±190	106.6±6.5	0.07063±0.00085	0.987±0.011	0.1518±0.0017	0.7861±0.0060	0.3837±0.0056	0.3252±0.0061
TVG1-10-1	Anh+Ba, 0.50910	C202	2850±230	129.9±8.1	0.07127±0.00083	0.9863±0.0074	0.1520±0.0011	0.7892±0.0052	0.3874±0.0027	0.3285±0.0033
<i>Mid-Atlantic Ridge near 13°S</i>										
S7-TVG4-2	Py, 0.59680	C189	142.6±7.2	9.79±0.70	0.0715±0.0031	0.984±0.010	0.1513±0.0032	0.787±0.013	0.3876±0.0049	0.3287±0.0083
<i>Kairei hydrothermal field, Central Indian Ridge</i>										
TVG9-1*	Py, 0.57712	C173	270±18	11.70 <sup>+0.83</sup> <sub>-0.61</sub>	0.0734±0.0027	0.984±0.012	0.1522±0.0019	0.788±0.012	0.3860±0.0065	0.3277±0.0054
TVG9-2*	Py, 0.57524	C174	455±30	16.6 <sup>+1.1</sup> <sub>-0.8</sub>	0.0732±0.0012	0.9828±0.0080	0.1514±0.0021	0.7873±0.0069	0.3874±0.0043	0.3285±0.0049
<i>Edmond hydrothermal field, Central Indian Ridge</i>										

TVG12-4 (I)*	Q, 0.79852	C175	1460±140	120±40	0.07094±0.00069	0.9800±0.0048	0.15174±0.00082	0.7872±0.0031	0.3874±0.0018	0.3286±0.0025
TVG12-4 (II)	Q, 0.25438	C176	1820±180	184±21	0.0714±0.0010	0.9835±0.0057	0.15209±0.00079	0.7883±0.0048	0.3877±0.0017	0.3292±0.0026
TVG12-5	Sp, 0.65574	K235	1290±110	59.1±4.3	0.0718±0.0018	0.989±0.018	0.1518±0.0099	0.7870±0.0067	0.3860±0.0057	0.3252±0.0070
TVG12-8	Sp, 0.66556	K232	157±11	9.14±0.75	0.0727±0.0017	0.987±0.023	0.1511±0.0042	0.793±0.011	0.3868±0.0097	0.326±0.013
TVG12-9	Sp, 0.65748	K233	301±22	15.2±1.2	0.0719±0.0031	0.989±0.021	0.1519±0.0031	0.7897±0.0086	0.3864±0.0065	0.3265±0.0090
TVG12-11	Sp, 0.64258	K234	161±11	8.27±0.62	0.0722±0.0025	0.989±0.023	0.1530±0.0056	0.790±0.015	0.386±0.011	0.3266±0.0095
TVG12-14	Sp, 0.66484	K236	155±12	8.41±0.82	0.0728±0.0039	0.993±0.027	0.1523±0.0042	0.795±0.017	0.388±0.012	0.327±0.010
TVG13-9.1	Anh/Ba, 0.60492	K239	754±82	35.9±3.8	0.0718±0.0017	0.990±0.017	0.1524±0.0029	0.790±0.012	0.3841±0.0051	0.3261±0.0082
TVG13-9.2	Py, 0.57428	C177	289±18	17.04±0.94	0.0732±0.0015	0.9813±0.0098	0.1522±0.0020	0.789±0.010	0.3876±0.0044	0.3271±0.0044
S18-TVG9	Py, 0.57318	C178	308±19	15.33±0.89	0.0729±0.0019	0.982±0.010	0.1520±0.0033	0.7868±0.0091	0.3868±0.0049	0.3268±0.0065
<i>A area, Southwest Indian Ridge</i>										
TVG22	Py, 0.60364	K237	251±18	14.5±1.2	0.0718±0.0025	0.990±0.018	0.1538±0.0037	0.797±0.011	0.3883±0.0082	0.3285±0.0087
<i>Southwest Indian Ridge near 63.5°E</i>										
S25-TVG21	Py, 0.59026	K238	1020±120	142±16	0.0724±0.0017	0.989±0.018	0.1520±0.0025	0.7916±0.0094	0.3871±0.0055	0.3259±0.0074
<i>Sonne 99 hydrothermal field, North Fiji Basin, Back-arc Basin</i>										
26.1GTV-1	Sp, 0.60020	C195	31.8±1.6	2.82±0.53	0.0705±0.0042	0.982±0.028	0.1498±0.0056	0.784±0.013	0.3881±0.0069	0.3294±0.0074
26.1GTV-2	Sp, 0.61818	C196	147.2±7.2	8.93±0.68	0.0714±0.0017	0.987±0.018	0.1524±0.0053	0.791±0.012	0.3891±0.0067	0.3308±0.0095
26.2GTV	Sp, 0.70824	C198	267±16	27.0±8.9	0.0716±0.0022	0.990±0.014	0.1518±0.0026	0.791±0.010	0.3883±0.0059	0.3289±0.0066
42GTV	Cpy+Py, 0.61930	C199	128±17	24 <sup>+31</sup> <sub>-24</sub>	0.0719±0.0025	0.987±0.015	0.1526±0.0042	0.789±0.012	0.3865±0.0064	0.3287±0.0070
113.1GTV	Cpy+Py, 0.60398	C200	545±33	68±21	0.0711±0.0017	0.9858±0.0097	0.1515±0.0020	0.7864±0.0096	0.3834±0.0047	0.3247±0.0074
113.2GTV	Py, 0.64228	C194	901±71	53.4±3.2	0.0713±0.0010	0.9871±0.0077	0.1516±0.0025	0.7919±0.0055	0.3863±0.0053	0.3275±0.0049
Atmosphere					0.07136	0.9832	0.15136	0.7890	0.3879	0.3293

Atmosphere data from Ozima and Podosek (2002).













