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HELIUM ISOTOPE COMPOSITION OF FLUID INCLUSIONS HOSTED IN MASSIVE SULFIDES FROM MODERN SUBMARINE HYDROTHERMAL SYSTEMS

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Abstract

Noble gas compositions of fluid inclusions hosted in sulfides from two modern submarine hydrothermal sites of contrasting tectonic settings have been analyzed. The JADE field (central Okinawa Trough, Japan) is located in an active intracontinental back-arc basin whereas the SO 134 field is related to the central spreading ridge of the north Fiji basin, which represents an active, highly mature intra-ocean back-arc system. Previous conventional studies of fluid inclusions have revealed compelling evidence for subcritical phase separation of the hydrothermal fluids at both sites. Elemental abundances of Ne, Ar, Kr, and Xe in fluid inclusions in all studied samples of chalcopyrite and sphalerite from both hydrothermal sites indicate that the heavier noble gases are derived from ambient seawater. In contrast, helium concentrations are 1 to 2 orders of magnitude higher than expected for equilibrium solution in seawater, indicating that helium is predominantly derived from a magmatic source beneath the hydrothermal systems. The $^3He/^4He$ ratios in sphalerite-hosted fluid inclusions from the JADE field and the SO 134 field are similar to those reported from related vent fluids and show that fluid inclusions reliably record the helium isotope ratio of the original hydrothermal fluid. However, in the north Fiji basin, earlier "black smoker" activity and the formation of Fe-rich "Kies-type" sulfides seems to have been related to a more MORB-like volcanism, whereas the younger recent "white smoker" hydrothermal activity in the north Fiji basin can be attributed to a hot spot magmatism in the study area.

Introduction

Extraction of volatiles from the ocean crust plays an important part in the geochemistry of modern submarine hydrothermal systems. In general, highly reactive gases (e.g., H_2, H_2S) that are controlled by fluid-mineral equilibrium are distinguished from supply-controlled gases such as He and CO_2 which are believed to be supplied to the systems by degassing from the magma chambers beneath the hydrothermal systems (e.g., Lupton et al., 1989, 1990; Baker and Lupton, 1990; Butterfield, 2000; Lilley et al., 2003).

Here we present an analysis of noble gases from fluids that were trapped in fluid inclusions hosted in sulfides from two active hydrothermal sites, namely the JADE field situated in the central Okinawa Trough and the north Fiji basin in the western Pacific Ocean (Fig. 1). At both sites, hydrothermal fluids underwent subcritical phase separation during ascent. The study aims to characterize the origin of noble gases in the sulfide-forming fluids and to compare the data with those obtained by direct analysis of vent fluids (Ishibashi et al., 1994, 1995).

Geologic Setting

The JADE field, hosted by intermediate to felsic volcanic rocks, is situated in the central Okinawa Trough, which extends from the island of Kyushu (Japan) in the northeast to Taiwan in the southwest (Halbach et al., 1989). This currently active intracontinental back-arc basin is related to the steep-angled subduction of the Philippine plate under the Eurasian plate. Tectonically, the Okinawa Trough is dominated by a number of large transcurrent fault systems, rotating blocks,

and horst and graben structures that are caused by oblique subduction (Kimura, 1985; Letouzey and Kimura, 1985). The JADE site is composed of active and inactive chimneys as well as mounds on the sea floor at a water depth between 1,300 and 1,550 m. High-temperature fluids emanating from chimneys show 50 to 100 times higher gas content of CO_2, H_2S, and CH_4 when compared with hydrothermal fluids from MORs (Sakai et al., 1990). Helium ratios of vent fluids range between 6.1 and 6.5 R_A (Ishibashi et al., 1995; R_A is the atmospheric $^3He/^4He$ ratio of 1.39×10^{-6}). He and CO_2 are considered to be derived from a magma chamber beneath the hydrothermal system, whereas CH_4 is assumed to be derived by decomposition of organic matter during the interaction of hydrothermal fluids with sediments (Ishibashi et al., 1995). The highest temperature of vent fluids emanating from a black smoker chimney was found to be 320°C (Sakai et al., 1990). The mineralization related to hydrothermal activity at the JADE field is assumed to be a modern analogue of the ancient Kuroko-type deposits (Halbach et al., 1989), and is made up of complex mineral assemblages, namely a sulfide-bearing sediment layer, two types of massive polymetallic sulfide, and a Pb-Zn-rich stockwork mineralization within hydrothermally altered magmatic host rocks.

The north Fiji basin, located in the southwest Pacific, is an active, highly evolved mature intra-ocean back-arc basin with ocean-floor basalts showing different geochemical signatures, i.e., N-MORB, alkali OIB, and less frequent E-MORB (e.g., Eissen et al., 1991; Lagabrielle et al., 1997; Seifert et al., 1998). The samples studied here originate from the SO 134 field, which is located in the central part of the north Fiji basin. Massive sulfides (chalcopyrite I, pyrite, marcasite, and sphalerite I with varying Fe content) deposited in mounds on

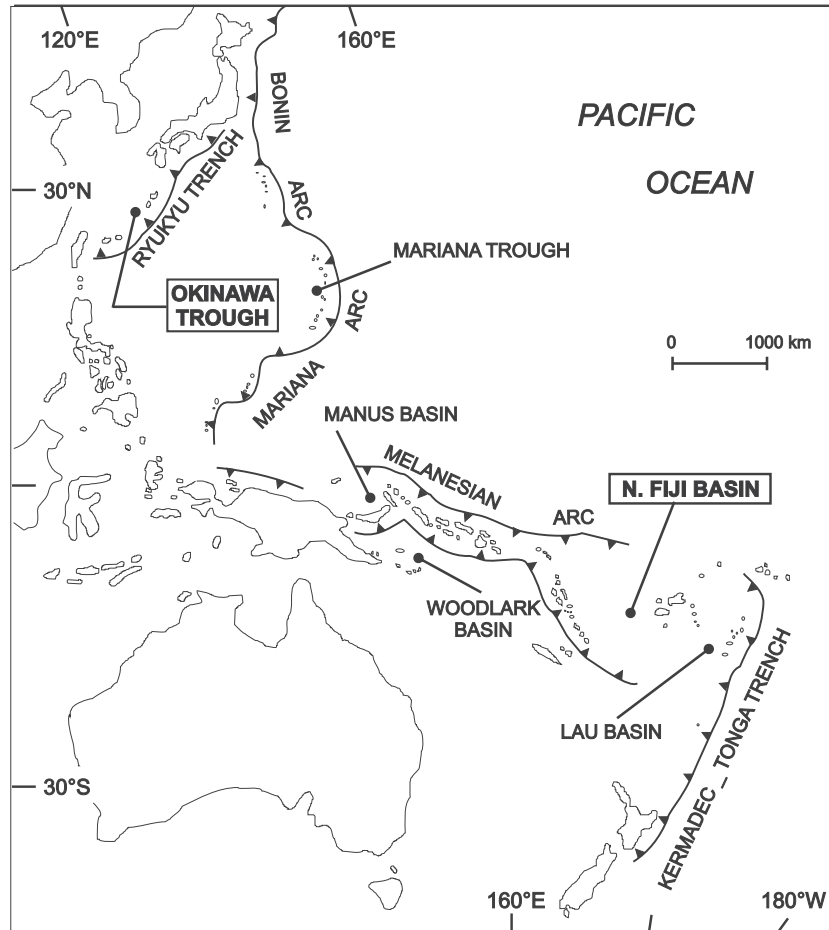[†] Corresponding author: e-mail, volue@gfz-potsdam.de

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FIG. 1. Location map of the western Pacific Ocean showing the locations of the Okinawa Trough and the north Fiji basin.

the sea floor from black smokers at a water depth of about 2,000 m (Halbach et al., 1999). During a later stage of mesothermal activity sphalerite II crystals and minor chalcopyrite II precipitated as replacement ore in the chimneys, thus indicating that the hydrothermal intensity has decreased from that associated with "black smokers" to "white smokers" (Halbach et al., 1999). The helium isotope ratios of vent fluids (Ishibashi et al., 1994) and basalts (Nishio et al., 1998; Marty and Zimmermann, 1999) range between 9.0 and 10.3 R_A and are somewhat higher than those typical for MORB worldwide (~8 ± 1 R_A; e.g., Hilton et al., 1993), indicating a more ^{3}He rich component in the North Fiji magmatic system.

Fluid Inclusion Characteristics

Microthermometric studies of sphalerite-hosted two-phase fluid inclusions from stockwork ores that deposited in the upper regions of subsea-floor upflow zones of hydrothermal fluids in the JADE field and in massive sphalerite mounds on the sea floor in the north Fiji basin have revealed compelling evidence for two-phase separation of seawater (Lüders et al., 2001, 2002). The salinity of primary fluid inclusions covers a large range from 1.5 to 15 wt percent NaCl equiv at the JADE site and from 3.2 to 10.5 wt percent NaCl equiv in the north Fiji basin. At the JADE site, heated seawater would undergo two-phase separation (Bischoff and Pitzer, 1985) at temperatures between 320° and 335°C, assuming pressure conditions between 130 and 155 bars to be controlled by the present water depth. The homogenization temperatures of fluid inclusions in sphalerite from the JADE Field indicate formation temperatures between 300° and 375°C (Lüders et al., 2001). Fluid inclusions yielding homogenization temperatures >340°C mostly show a salinity below that of seawater (~3.2 wt % NaCl equiv), suggesting condensation of a low-salinity vapor phase. Fluid inclusions hosted in sphalerite from the JADE field show Cl/Br ratios less than that of seawater (Fig. 2) indicating significant loss of Cl by boiling of the ascending hydrothermal fluids and/or halite precipitation at depth. The Na/Br ratios of most of the JADE field fluids plot left of the seawater evaporation line and indicate exchange of Na for other cations by water-rock interaction of the hydrothermal fluids with the felsic rocks. This could be, for example, Ca if interaction with plagioclase is involved (Davisson and Criss, 1996) or K if albitization of K-feldspar has taken place (Banks et al., 2002). Since fluid inclusions in sphalerite from the JADE field are extremely enriched in K (Lüders et al., 2002), K-feldspar alteration of the felsic volcanic rocks by the hydrothermal fluids seems to be likely, similar to K enrichment and Na depletion of hydrothermal vent fluids at the Juan de Fuca Ridge (Butterfield et al., 1990).
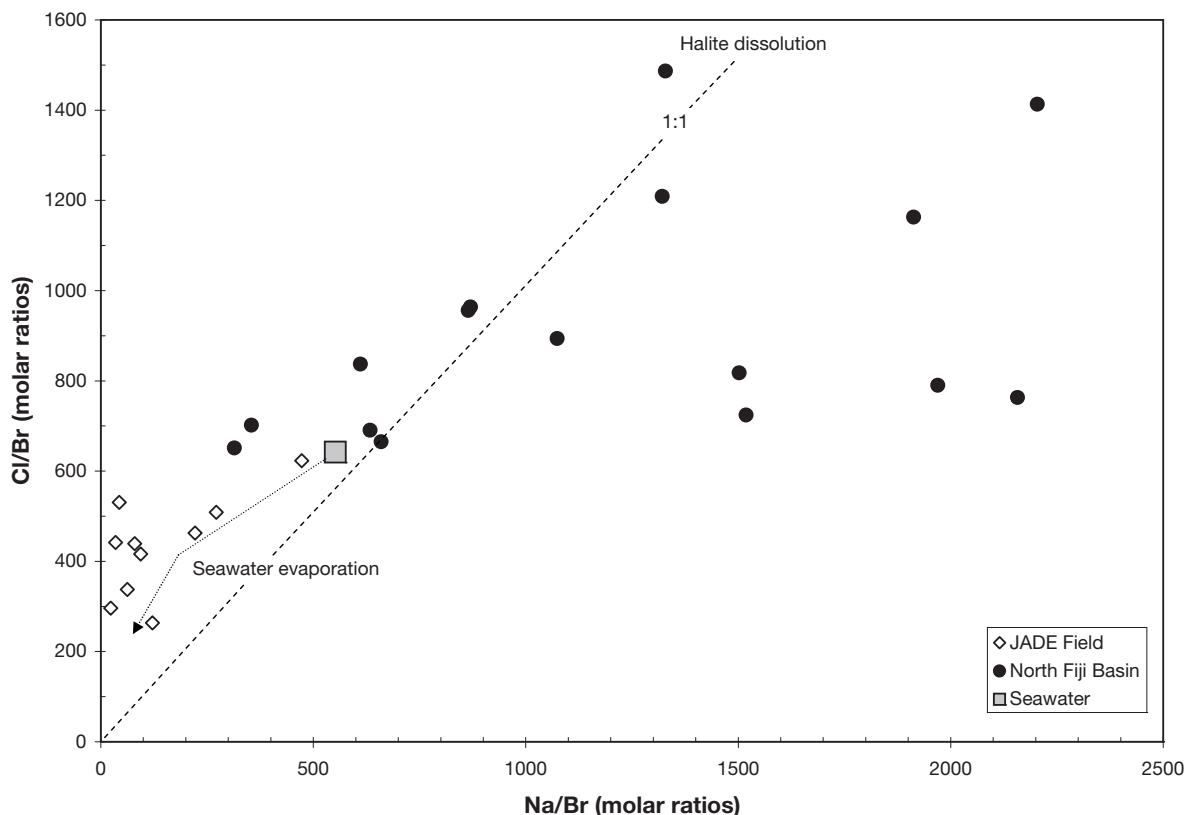
FIG. 2. Na/Br and Cl/Br molar ratios of sphalerite-hosted fluid inclusions relative to evaporation of seawater and dissolution of halite. Data taken from Lüders et al. (2002).

At the Fiji site, the Cl/Br ratios of sphalerite-hosted inclusions are mostly higher than the Cl/Br ratios of seawater (Fig. 2), which may be indicative for dissolution of halite. Some samples are depleted in Na but not enriched in K (Lüders et al., 2002) when compared with seawater, indicating albitization of basaltic rocks during water-rock interaction. However, a couple of samples are enriched in Na with respect to seawater, probably due to chloritization and/or alteration of alkaline (OIB) basalts. The homogenization temperatures of sphalerite-hosted fluid inclusions that are attributed to "white smoker-type mineralization" are significantly lower (max 260°C), indicating a process of conductive cooling combined with subsurface storage of the ore-forming fluids prior to sphalerite deposition (Lüders et al., 2002). The presence of fluid inclusions in chalcopyrite from black smoker mineralization has been demonstrated by infrared microscopy. However, although most of the studied samples of chalcopyrite show patchy transparency under near-infrared radiation, fluid inclusions therein always appear dark (Fig. 3), as previously also observed for pyrite-hosted fluid inclusions (e.g., Richards and Kerrich, 1993; Lüders and Ziemann, 1999) probably due to intense refraction of light resulting from the high refractive contrast between chalcopyrite and aqueous fluids. Therefore, no microthermometric fluid inclusion measurements in chalcopyrite were possible.

Experimental Procedure and Results of Noble Gas Analyses

Samples of 0.67 to 2.15 g of sphalerite and chalcopyrite (Table 1) were loaded into an ultrahigh-vacuum spindle crusher, which was baked at 100°C for 24 h to remove atmospheric gases adsorbed on grain surfaces. For gas extraction the samples were squeezed between two hard metal jaws, and the gases released from fluid inclusions were admitted to the preparation line. Water was frozen to a dry ice-cooled trap and other chemically active species were removed in Ti sponge and ZrAl getters. Noble gases were then separated from each other in a cryogenic adsorber, and noble gas concentrations and isotopic compositions were determined in a VG5400
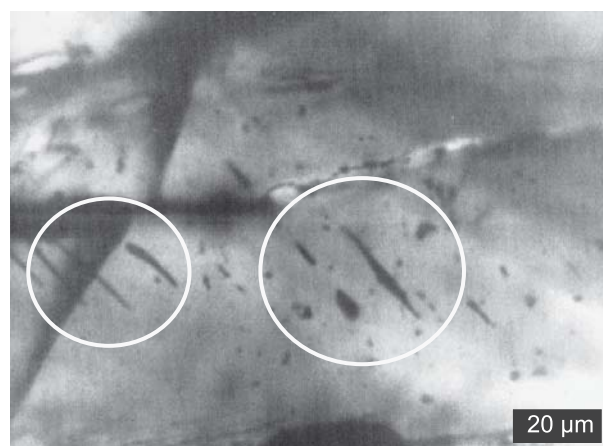

FIG. 3. Photomicrograph in infrared light of opaque fluid inclusions hosted in chalcopyrite from "Kies"-type mineralization of the SO 134 field, north Fiji basin.

TABLE 1. Noble Gas Concentrations (cm³ STP/g) and ³He/⁴He Ratios (RA) in Sphalerites (sph) and Chalcopyrites (chp)
from the Jade Field and North Fiji Basin

Sample Weight	⁴He 10^{-8}	²⁰Ne 10^{-12}	⁴⁰Ar 10^{-8}	⁸⁴Kr 10^{-12}	¹³²Xe 10^{-12}	³He/⁴He R_A
Jade field						
H-1 sph	0.260	393	32.1	24.1	1.039	5.66
0.9716 g	±0.018	±24	±2.4	±1.5	±0.066	±0.67
160 DSE-1a sph	0.601	1520	113.5	88.6	3.49	5.75
1.0793 g	±0.048	±130	±9.5	±6.3	±0.29	±0.54
160 DSE-1b sph	0.579	1310	102	84.0	4.03	5.74
1.0379 g	±0.058	±110	±11	±6.8	±0.40	±0.50
North Fiji basin						
42.3 B chp I	0.130	78.8	9.37	9.66	0.592	8.6
0.8002 g	±0.013	±6.4	±0.94	±0.80	±0.058	±1.8
42.3 D chp I	0.235	142.4	18.9	16.9	0.827	8.60
2.0915 g	±0.012	±7.2	±1.3	±2.3	±0.049	±0.44
Kleinmassiv chp I	0.189	189	15.40	16.1	1.18	8.75
1.0550 g	±0.013	±12	±0.77	±1.3	±0.13	±0.68
Plate xx chp I	0.180	184	16.4	17.6	1.74	8.9
1.2217 g	±0.011	±14	±1.2	±1.6	±0.14	±1.0
Corner Mt./Druse Rim chp I	0.763	757	57.1	45.7	2.43	9.12
0.6740 g	±0.046	±56	±4.8	±3.3	±0.18	±0.84
Corner Mt. 1 chp I	0.877	1304	98.2	78.0	4.16	9.29
1.1436 g	±0.053	±97	±8.2	±5.6	±0.49	±0.63
42.3 A chp II	1.376	1134	72	61	7.2	10.82
2.1537 g	±0.069	±62	±41	±48	±6.7	±0.43
42.3 C chp II	0.858	559	57.6	45	4.80	9.64
1.4588 g	±0.043	±29	±4.6	±21	±0.93	±0.69
DSE 26-10 sph II	0.231	117.1	45.1	34.9	1.697	9.7
0.9709 g	±0.012	±7.2	±3.1	±1.8	±0.090	±1.1
26 GTV sph II	0.299	227	61.1	44.8	2.15	9.36
1.4079 g	±0.015	±14	±4.2	±2.3	±0.12	±0.52
26 GTV xx sph II	0.493	176	16.12	17.01	1.25	9.49
0.9906 g	±0.030	±11	±0.82	±0.86	±0.19	±0.80
HB sph II	0.302	208	45.7	34.6	1.442	10.4
1.5270 g	±0.015	±11	±3.1	±1.7	±0.074	±1.2

Notes: At north Fiji basin, types I and II mineralization are distinguished as related to black and white smoker activity, respectively; ³He/⁴He ratios have been corrected for a minor atmospheric component from ambient seawater, according to Craig et al. (1978); the corrections are <7% for all samples; error limits are 2σ

noble gas mass spectrometer according to procedures described earlier (Niedermann et al., 1997). In order to characterize the noble gas composition of recent magmatic fluids, two basalt glasses from the north Fiji basin were also studied both by crushing and stepwise heating (at 400°, 800°, and 1500°C) in a double-walled, resistance-heated furnace. Procedural blanks were measured before each sample gas extraction. Total blank ranges (in units of 10^{-12} cm³ STP) for the sample suite were 2 to 40 for ⁴He, 0.3 to 2.0 for ²⁰Ne, 200 to 2,000 for ⁴⁰Ar, 0.02 to 0.18 for ⁸⁴Kr, and 0.006 to 0.08 for ¹³²Xe.

In Tables 1 and 2, noble gas concentrations of sphalerite and chalcopyrite as well as glass samples are shown along with ³He/⁴He ratios. Isotopic compositions of Ne, Ar, Kr, and Xe are atmospheric throughout, except for Ne and Ar in the glass samples. All data in the tables have been corrected for relevant blank values, mass discrimination and isobaric interferences, and are given with uncertainties corresponding to 95 percent confidence level.

The noble gas concentrations reported in Table 1 are not really absolute, in the sense that the crushing technique does not open all fluid inclusions. The crushing efficiency depends on factors such as original grain size, size of fluid inclusions, and mineral hardness. For common minerals such as quartz or olivine, it is typically between 50 and 100 percent in our lab. Jean-Baptiste and Fouquet (1996), who used a crusher very similar in design to ours, determined crushing efficiencies of ~60 percent for chalcopyrite, but only 12 to 20 percent for a sample dominated by sphalerite, pyrite, and marcasite. In the following, we do not discuss absolute noble gas concentrations but only elemental and isotopic ratios, which are not expected to be affected by crushing efficiencies.

Our results for two north Fiji basin basalt glasses (Table 2) show ³He/⁴He ratios of 8.9 to 9.4 R_A, similar to those reported earlier from this location (Nishio et al., 1998; Marty and Zimmermann, 1999), which indicates the involvement of a plume-type component in the magmatic activity. In Figure 4, we report the first neon isotope data for the north Fiji basin. They are consistent with that interpretation, as despite atmosphere-like compositions or large uncertainties for most measurements, at least the 800°C step of 25GTV8 plots unequivocally between the MORB (Sarda et al., 1988) and Loihi-Kilauea (Honda et al., 1991) correlation lines in the Ne three-isotope diagram (Fig. 4), as expected for a mixture of MORB- and plume-like components.

TABLE 2. Noble Gas Concentrations (cm³ STP/g) and ³He/⁴He Ratios (RA) in Two Basalt Glasses from North Fiji Basin

Sample Weight		⁴He 10^{-8}	²⁰Ne 10^{-12}	⁴⁰Ar 10^{-8}	⁸⁴Kr 10^{-12}	¹³²Xe 10^{-12}	³He/⁴He 10^{-8}
99GTV cr		367	150.3	12.02	7.52	0.571	9.34
0.8031 g		±26	±7.7	±0.61	±0.38	±0.047	±0.34
99GTV sh	*400°C*	7.06	59.0	2.61	2.27	0.167	9.96
0.5069 g		±0.25	±3.1	±0.15	±0.14	±0.047	±0.74
	800°C	637	538	31.3	19.7	2.11	9.40
		±23	±27	±1.8	±1.2	±0.60	±0.11
	1500°C	0.904	7.0	0.97	1.84	2.19	8.7
		±0.046	±1.2	±0.36	±0.39	±0.38	±3.5
	Total	645	604	34.9	23.8	4.47	9.41
		±23	±27	±1.8	±1.3	±0.71	±0.11
25GTV8 cr		617	144.9	41.8	8.10	0.630	8.86
0.09719 g		±31	±8.2	±2.2	±0.45	±0.080	±0.25
25GTV8 sh	*400°C*	46.9	21.5	1.002	1.001	0.169	9.58
0.5048 g		±1.7	±1.3	±0.083	±0.090	±0.048	±0.17
	800°C	1615	225	60.1	6.37	1.43	9.17
		±57	±11	±3.0	±0.37	±0.13	±0.10
	1500°C	5.50	21.1	12.40	2.71	0.91	7.59
		±0.20	±1.6	±0.60	±0.24	±0.20	±0.58
	Total	1667	268	73.5	10.08	2.51	9.18
		±57	±11	±3.1	±0.45	±0.24	±0.10

Notes: Gas extraction was performed by both crushing (cr) and stepwise heating (sh); error limits are 2σ

Discussion

Elemental abundances of Ne, Ar, Kr, and Xe in fluid inclusions in all studied samples of chalcopyrite and sphalerite from both hydrothermal sites are similar to those in air-saturated water (Fig. 5). This indicates that the heavier noble gases are derived from ambient seawater, which is also supported by their atmospheric isotopic compositions. In particular, the three samples from the JADE field (only two are shown in Fig. 5) plot very close to the 250°C equilibrium solution line, which is reasonably similar to the fluid inclusion
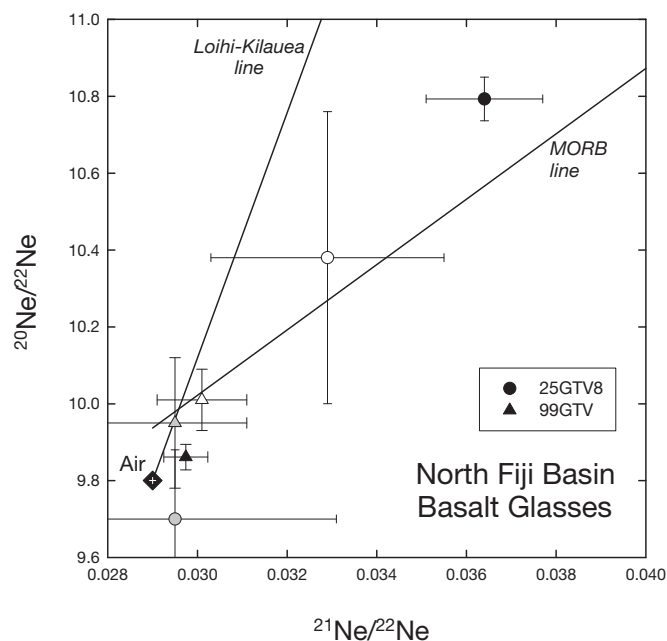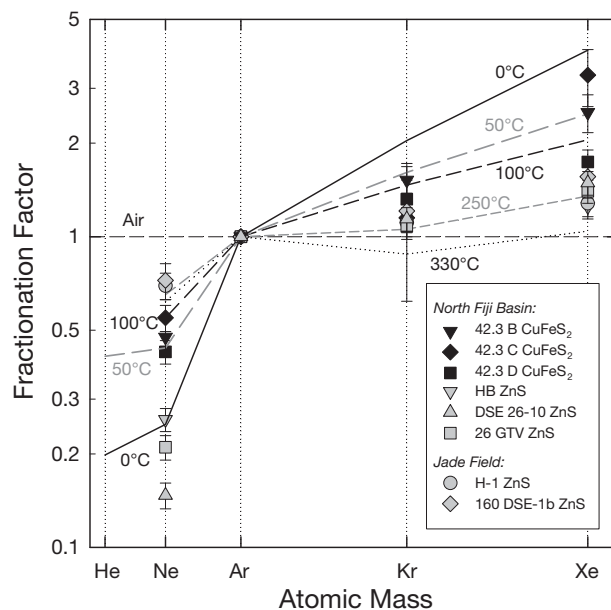

FIG. 4. Neon three-isotope plot for two basalt glasses from North Fiji Basin. White symbols show crushing extractions, gray symbols = 400°C, and black symbols = 800°C heating steps. Data for 1500°C steps are not shown because of an excessive isobaric interference from CO_2^{++} to the ²²Ne measurement. The MORB and Loihi-Kilauea lines are mixture lines between an atmosphere-like component and components characteristic of MORB and Hawaiian plume magmas, respectively (Sarda et al., 1988; Honda et al., 1991). The position of data points (in particular, 25GTV8 800°C) between those lines is thus indicative of an involvement for both MORB- and plume-related components.

FIG. 5. Elemental abundance ratios of noble gases, expressed as fractionation factor F relative to atmospheric abundance and ⁴⁰Ar. F is defined as $(^iX/^{40}Ar)_{sample}/(^iX/^{40}Ar)_{air}$, where ^iX is a noble gas isotope. Fractionation patterns for dissolution equilibrium of noble gases in water are given for 0° and 50°C at 5 percent salinity according to Smith and Kennedy (1983), and for 100°, 250°, and 330°C, according to Crovetto et al. (1982). The samples shown are representative for the whole sample suite. He data are not displayed because they would plot well above the range shown.

homogenization temperatures. It must be noted that the high-temperature (100°, 250°, and 330°C) equilibrium solution lines in Figure 5 (taken from Crovetto et al., 1982) do not take into account the salinity of the water because solubility data for noble gases in saline water are not available for this temperature range. Among the north Fiji basin samples, the chalcopyrites are generally consistent with equilibrium solution at distinctly lower temperatures between ~50° and 100°C (e.g., 42.3 B, 42.3D), whereas most sphalerites show a clear depletion of Ne with respect to the heavier noble gases. Even though the reason for this latter observation is not clear, the differences in elemental abundance ratios among distinct samples are most probably related to varying equilibration temperatures and salinities as indicated by fluid inclusions microthermometry.

Helium concentrations are one to two orders of magnitude higher than expected for equilibrium solution in seawater, indicating that He is predominantly derived from a magmatic source beneath the hydrothermal systems. The ^{3}He/^{4}He ratios in fluid inclusions from the JADE field (Table 1; Fig. 6), corrected for a <7 percent contribution of seawater He, are similar to those reported from vent fluids (Ishibashi et al., 1995) and show that noble gases in fluid inclusions are representative for the origin of hydrothermal fluids. This finding is in good agreement with earlier studies (Jean-Baptiste and Fouquet, 1996). Sphalerite from the stockwork mineralization of the JADE field formed at temperatures well above 300°C (Lüders et al., 2001). Varying salinity and Cl/Br ratios lower than that of seawater suggest boiling of the parental ore-forming fluid beneath the site of mineralization. The He isotope ratio of ~5.7 R_A of sphalerite-hosted fluid inclusions is typical for hydrothermal sites related to island arc magmatism (Sano and Wakita, 1985). Helium signatures of about 6 R_A are lower than those of MORB (~8 ± 1 R_A; Hilton et al., 1993) and are assumed to be affected by contamination with crustal

components and/or subducting material (Sano and Wakita, 1985).

The samples from the north Fiji basin show two distinct trends; fluid inclusions hosted in chalcopyrite I samples that are related to "black smoker" activity tend to have lower ^{3}He/^{4}He ratios when compared with fluid inclusions hosted in sulfides that are related to "white smoker" activity (Fig. 6). The latter show ^{3}He/^{4}He ratios clearly higher than average MORB and are similar to vent fluids from anhydrite chimneys from an active hydrothermal vent site located on the central ridge of the north Fiji basin (Ishibashi et al., 1994). The helium isotope composition of vent fluids and fluid inclusions in minerals that deposited from white smoker hydrothermal fluids in the range between 9 and 11 R_A indicates a ^{3}He-rich, plume-like component in the magmatic system of the central north Fiji basin. Trace element distribution and isotope ratios of basalts suggest that basalts from the northern part of the central ridge derived from a mixed N-MORB and OIB-type source (Eissen et al., 1994; Nohara et al., 1994). Alkali OIB-type basalts are frequent beside N-MORB-type basalts in the SO 134 field and may be indicative of a local hot spot magmatism (Halbach et al., 1999). High ^{3}He/^{4}He ratios and plumelike Ne isotope compositions were also found in glasses from OIB-type in the study area (Table 1; Fig. 4) and support a genetic relationship between hot spot magmatism and the younger hydrothermal activity in the study area. Varying salinity of two-phase fluid inclusions in sphalerite II between 3.2 (seawater salinity) and 10.5 wt percent NaCl equiv (Lüders et al., 2002) as well as variable Cl/Br ratios (Fig. 2) either suggest dissolution of halite at depth or mixing of seawater with magmatic brines (Cl/Br molar ratios ≈ 500–1,500) to varying degrees. However, the precursory older "black smoker" activity and the formation of Fe-rich "Kies-type" sulfides seem to be related to a more MORB-like volcanism as indicated by lower ^{3}He/^{4}He ratios of fluid inclusions hosted in chalcopyrite I (Table 1).

Conclusion

The helium isotope composition of fluid inclusions hosted in massive sulfides from modern submarine hydrothermal sites is similar to that of vent fluids from which they deposited. Therefore, noble gases in fluid inclusions are representative for the origin of hydrothermal fluids. The study of fluid inclusions hosted in types of mineralization that are different from the north Fiji basin also shows that fluid inclusions provide a tool to examine fossil hydrothermal systems and to discriminate sources of helium.

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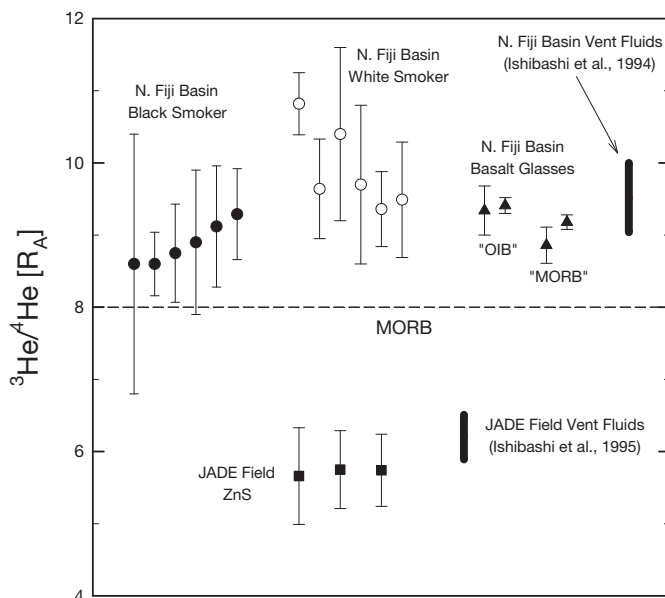
FIG. 6. ^{3}He/^{4}He ratios from all samples of this study, in comparison to the typical MORB value of 8 R_A and to data from vent fluids at the respective sampling locations (Ishibashi et al., 1994, 1995).

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