19. HELIUM AND SULFUR ISOTOPES OF SULFIDE MINERALS FROM MIDDLE VALLEY, NORTHERN JUAN DE FUCA RIDGE¹

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ABSTRACT

The noble gas composition of fluids trapped in sulfides at Ocean Drilling Program Leg 139, Site 856, were measured. Helium in these fluids is significantly enriched relative to deep oceanic waters but is considerably lower than the helium contents of mid-ocean ridge (MOR) vent waters and fluid inclusions in sulfide minerals from 21°N on the East Pacific Rise. Sulfide ³He⁴He ratios, corrected for air using He/Ne ratios, are between 5.8 and 7.1 times the air value (R_a). These ratios are lower than those of typical MOR vent fluids (~8 R_a), and are closer to those of vent waters from the sediment-covered Guaymas Basin because of the dilution of a normal MOR He component by radiogenic He. The radiogenic He may be derived either from sedimentary pore fluids or from aging of the magmatic system beneath the northern Juan de Fuca Ridge. Low He abundances precluded sufficiently accurate ³He⁴He measurements to identify subtle depth variations that could be used to understand temporal evolution of the hydrothermal system. A broad negative $\delta^{34}S_{-}^{-3}He^{4}$ He trend is identified that is consistent with a sedimentary origin for the radiogenic He at Middle Valley. ⁴⁰Ar/³⁶Ar and Xe isotope ratios imply an atmospheric origin for the heavy noble gases that probably originate in minor hydrated minerals, which precludes the determination of absolute abundances of He in the fluid inclusions.

INTRODUCTION

Isotopic measurements of helium in oceanic basalts (Lupton and Craig, 1975; Kurz et al., 1982; Allègre et al., 1983) have shown that the mantle beneath the global mid-ocean ridge (MOR) system is characterized by a uniform composition. 3 He/ 4 He ratios display a narrow range, between 8 and 10 times the atmospheric value (R_a), and are three orders of magnitude greater than that of radiogenic helium (e.g., Morrison and Pine, 1955) that characterizes the continental crust. The distinctive composition of upper mantle He is widely considered to be what remains of the primordial gases after the degassing of a significant portion of the Earth's interior (Allègre et al., 1983). The low 3 He production rate in the continental crust and the low abundance of He in the atmosphere allows the detection of small additions of mantle-derived 3 He to surface fluids (see Lupton, 1983a, for review).

Extensive surveys have revealed excesses of ³He in the water column above mid-ocean ridges (e.g., Craig et al., 1975; Jenkins et al., 1978; Lupton et al., 1980), at sites of extension of the oceanic crust (Lupton, 1979), and at sites of intraplate volcanism (Horibe et al., 1983; Kodera et al., 1988). The recognition that "primordial" He is scavenged from recently emplaced oceanic crust and released in plumes of hot (metal-rich) waters (Craig et al., 1975) supports models of hydrothermal circulation of seawater previously proposed to account for the low conductive heat flow at ridge crests, the $\delta^{18}O$ depletions in ocean floor and ophiolitic basalts, and the presence of metalliferous sediments at Pacific ridge crests. Subsequent detailed chemical studies showed that the hydrothermal end-member solutions (350°C) can be enriched in ³He by in excess of 20,000 times that of ambient seawater (Butterfield et al., 1990). 14C-based estimates of the residence time of ³He in the oceans allowed Craig et al. (1975) to calculate the flux of mantle-derived He from the solid Earth, which has subsequently been used to estimate the global fluxes of many other elements (see Le Cloarec and Marty, 1991, for review). Early studies of ridge-crest hydrothermal systems revealed rather constant He/heat ratios from which Jenkins et al. (1978) calculated the global hydrothermal heat flux from the oceans to be 2×10^{-20} J/yr, close to independent estimates made from geophysical considerations. However, more recent work suggests that He concentrations and ³He/heat ratios in hydrothermal systems vary on short time scales (Lupton et al., 1989; Baker and Lupton, 1990). This is most likely to occur in response to fundamental tectonomagmatic processes occurring at midocean ridges (Baker and Lupton, 1990), and the apparent global uniformity of ³He/heat ratios probably represents hydrothermal systems at equilibrium.

He isotope information, until now available only from the study of vent fluids, was recently acquired by *in vacuo* crushing of sulfide minerals from chimneys at 21°N on the East Pacific Rise (EPR) (Turner and Stuart, 1992). The ³He/⁴He ratios in these samples is identical to that of the vent waters, whereas Ar, Kr, and Xe abundances and isotopes imply that the heavy noble gases are derived from an atmospheric source. ³He/³⁶Ar ratios provide information on the degree of water-rock interaction and reveal a perceptible enrichment of He in the trapped fluids over that measured in contemporary vent fluids. This may reflect the evolution of ocean-floor hydrothermal systems similar to the one detected in the "megaplume" over the Juan de Fuca Ridge in 1986 (Baker et al., 1987). However, we cannot rule out the possibility that the trapping of vent fluids fractionates the noble gases.

Here we present the results of a study of the He and Ne trapped in fluid inclusions within pyrite from the massive sulfide discovered at Site 856 on the Juan de Fuca Ridge during Ocean Drilling Program (ODP) Leg 139. ³He/⁴He ratios are used to constrain the origin of the hydrothermal fluid by allowing a direct comparison with ³He/⁴He ratios determined for vent fluids from other ridge-crest hydrothermal systems. Samples from different depths have also been analyzed in an attempt to place constraints on the He isotope evolution of an ocean-floor hydrothermal system.

SAMPLES AND EXPERIMENTAL PROCEDURE

We determined the noble gas composition of fluids trapped in pyrite and pyrrhotite from Holes 856G and 856H at the massive sulfide deposit at Middle Valley, northern Juan de Fuca Ridge. Sample nomenclature, mineralogy, and chemistry are reported in Table 1. A more detailed discussion of the mineralogy and sulfur isotope composition of these samples is presented by Duckworth et al. (this volume). Sample mineralogy given here was determined by powder X-ray diffraction (XRD) at the University of Manchester.

¹ Mottl, M.J., Davis, E.E., Fisher, A.T., and Slack, J.F. (Eds.), 1994. *Proc. ODP*, *Sci. Results*, 139: College Station, TX (Ocean Drilling Program).

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Table 1.	Depth and	mineralogy	of Site 856	samples.
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Core, section,	Depth (mbsf)	Mineralogy ^a		Pyrite ^b 834S
interval (cm)		Major	Minor	(%)
139-856H-				
2R-1, 4-6	13.54	Py Sd	Tc	+1.7
3R-3, 83-85	25.54	Py Pyh	Sd Go Sep Chl	+5.9
4R-2, 57-59	28.67	Py Mag	Pyh Chc Chl	+8.0(+7.6)
6R-1, 32-34	37.72	Py Mc	Cpy Mag Pyh Cal Dol	(+5.7)
10R-1, 8-10	57.08	Py	Cpy Serp Chl	+8.4
11R-1, 94-96	62.24	Py	Cpy Serp	+4.8
13R-1, 56-57	71.46	Py Mc	Mag Sd Pyh Dol Cal	+2.8
17R-1, 2-4	90.12	Py Pyh	Cpy Mag Go Serp Chl	+1.6
139-856G-				
7R-4, 6-8	60.16	Py Sph	Cpy Serp	+5.8

^a Py = pyrite, Pyh = pyrrhotite, Mag = magnetite, Mc = marcasite, Sd = siderite, Cpy = chalcopyrite, Sph = sphalerite, Chc = chalcocite, Serp = serpentine, Chl = chlorite, Cal = calcite, Dol = dolomite, Go = goethite, Tc = talc, Sep = sepiolite.

^b Values for pyrrhotite are in parentheses; δ³⁴S data are from Duckworth et al. (this volume).

Sulfide minerals were hand-picked from coarsely crushed hand specimens in an attempt to minimize contamination by hydrated minerals. From 300 to 500 mg of 0.5- to 2-mm-sized grains were loaded into the extraction apparatus and crushed sequentially *in vacuo* in a system of on-line crushers to preferentially release noble gases from fluid inclusions. The presence of H₂O in talc, serpentine, and chlorite required baking all the samples at approximately 200°C for 48 hours until the pressure in the crushing apparatus was <10⁻⁸ torr. Previous experiments have shown that noble gas loss from sulfide minerals at these temperatures is negligible (Turner and Stuart, 1992). The sample weights (Table 2) represent the fraction remaining after crushing that passed through a 100-µm-mesh sieve.

Extraction and gas processing were performed in a low-volume, all-metal line. The gases released were exposed to an SAES NP10 Al-Zr getter at 300°C for 20 min to remove the reactive gases. Heavy noble gases were then condensed onto a liquid N₂-cooled charcoal finger (VTC 1). Significant quantities of water remained at this stage, and required exposure of the residual gases to a second hot Al-Zr getter for a further 10 minutes before analyses of He and Ne. A cold C50 Ti-Zr getter and a second liquid N₂-cooled charcoal finger, adjacent to the spectrometer source, were employed during analysis to minimize the pressures of H and Ar, respectively. During He-Ne analysis the heavy noble gases were released from the VTC 1 at 100°C and subsequently admitted to the spectrometer for measurement of Ar isotopes and the abundances of Kr and Xe. In many cases, the abundances of the heavy noble gases were too high to measure; those cases are not discussed in detail here.

An all-metal MAP 215 mass spectrometer with a resolving power of >850 capable of complete resolution of the ³H-HD⁺ doublet from ³He⁺, was used for noble gas measurements. The low ³He/⁴He ratios in nature require measurement of ³He and ⁴He on electron multiplier and Faraday detectors, respectively. 3He/4He ratio measurements were calibrated against those made on 1.05×10^{-6} cm³ standard temperature and pressure (STP) air and have an overall reproducibility of ±5%. He/Ne ratios and absolute abundances of ⁴He and ²⁰Ne were made by peakheight comparison with this same amount of gas and have a reproducibility of $\pm 5\%$ (1 σ). The reproducibility of measuring small volumes of high ³He/⁴He gas was monitored by repeated crushes of an internal standard: a gas-rich olivine from a dunite xenolith from Réunion Island, Indian Ocean (R/R_a = 12.9 ± 0.06 , n = 10). A correction for the effect of ${}^{40}\text{Ar}^{2+}$ to mass 20 (0.2 ± 0.05) was made to ${}^{20}\text{Ne}$ abundances. Blank measurements were made by crushing inclusion-free quartz and were insignificant relative to gas amounts released by the sulfides.

RESULTS

³He/⁴He ratios and abundances of He and Ne of all samples are displayed in Table 2. He abundances are low compared with those for

Table 2. He and Ne data for Middle Valley sulfides from Site 856.

Core, section, interval (cm)	Weight (g)	4He (10 ⁻⁸ cm ³ /g)	R/R _a	²⁰ Ne (10 ⁻⁹ cm ³ /g)	(R/R _a) _{cor}
139-85611-					
2R-1, 4-6	0.134	0.16 ±0.02	nm	nm	nm
3R-3, 83-85	0.159	0.23 ±0.01	4.38 ±0.4	nm	nm
4R-2, 57-59	0.149	0.54	6.86 +0.5	0.7 ± 0.1	7.13 ±0.5
10R-1, 8-10	0.159	2.79	5.2 +0.28	10.7	5.83
11R-1, 94-96	0.413	3.66	5.74	5.5	5.98 ±0.2
13R-1, 56-57	0.141	0.26	6.2	0.4	6.48 +0.5
17R-1, 2-4	0.481	3.3	6.44	3.7	6.65 +0.14
139-856G-		10.01	10.14	10.2	10.14
7R-4, 6-8	0.152	1.61 ±0.04	5.66 ±0.24	2.5 ±0.1	5.9 ±0.24

Notes: R is the measured ³He/⁴He ratio, R_a is the equivalent value for atmosphere (1.4×10^{-6}) . (R/R_a)_{cor} is the measured value corrected for atmospheric He by assuming all Ne is of atmospheric origin using: (R/R_a)_{cor} = [(R/R_a)_{meas} × (X - 1)] / [X - 1], where X = (⁴He)²⁰Ne)_{meas}/(⁴He/²⁰Ne)_{air}He and Ne abundances are subject to a ±5% uncertainty (1 σ). nm = not measured.

sulfide minerals from 21°N EPR (Stuart et al., 1992; Turner and Stuart, 1992), resulting in imprecise 3 He/ 4 He measurements in a number of cases. Although 4 He/ 20 Ne ratios (2.6 to 9.1) indicate significant He enrichments over the atmospheric gas (0.31), they are lower than those of typical MOR vent fluids (e.g., Lupton et al., 1980; Kennedy, 1988). The highest He abundances were measured from coarse-grained sulfides (Samples 139-856H-17R-1, 2–4 cm and 139-856H-11R-1, 94–96 cm). We suppose that the low He abundances are a result of poor trapping of fluid inclusions by the fine-grained sulfides.

Sulfide ³He/⁴He and ²⁰Ne/⁴He ratios are plotted in Figure 1. The data lie slightly below a mixing line between atmospheric He and a MOR basalt component, indicating the presence of a small amount of radiogenic He in the trapped fluids. There are three possible sources of the atmospheric component: air contamination, modified seawater in fluid inclusions, and atmospheric gases in hydrated minerals. Minor amounts of air-derived noble gases are present in many analyses of solid samples (e.g., Böhlke et al., 1989; Böhlke and Irwin, 1992; Turner and Stuart, 1992). These noble gases may be adsorbed onto fresh mineral surfaces or implanted during sample preparation. It is difficult to determine the origin of the atmosphere-like component using light noble gas data alone. However, a correction for the atmospheric component can be made to the helium isotope data using the measured He/Ne ratio (Table 2). Because the solubilities of He and Ne in water within the expected temperature and salinity ranges are similar, the corrected ³He/⁴He ratios are insensitive to the origin of the atmospheric gases.

Corrected ³He/⁴He ratios range between 5.8 and 7.1 R_a. Using end-member values of 8.4 R_a for MOR basalt He (Trull et al., 1990) and 0.02 R_a for radiogenic He produced in deep-sea sediments (Sano and Wakita, 1986) between 15% and 33% of the ⁴He in these samples is of radiogenic origin. ³He/⁴He ratios are plotted in Figure 2 along with data from submarine hydrothermal vent waters, 21°N EPR sulfides, and oceanic basalts. The measured He isotope ratios are below those of vent fluids from the Juan de Fuca Ridge (see Lupton et al., 1989). The young age of the Middle Valley sulfide deposit rules out in-situ ⁴He as an important contribution in these samples.

³He/⁴He ratios of submarine vent fluids are commonly slightly lower than those of nearby basalts (e.g., Kennedy, 1988; Kodera et al., 1988; but see Craig and Lupton, 1981). Differences in the ³He/⁴He ratios of MOR basalts and hydrothermal fluids venting along the Juan de Fuca Ridge have been suggested to result from the addition of radiogenic ⁴He (here termed ⁴He_{RAD}) to hydrothermal fluids during seawater circulation in the oceanic crust (Kennedy, 1988). However,



Figure 1. Air-normalized He isotope ratios (R/R_a) and ²⁰Ne/⁴He ratios for Middle Valley sulfides. The Middle Valley data are displayed as open circles; end-member noble gas components (air, MORB, and radiogenic) are filled squares. The mixing line is drawn between air (R/R_a = 1) and MORB (R/R_a = 8.4, ²⁰Ne/⁴He = 5×10^{-5} : "popping rock" from Staudacher et al., 1989). The data plot slightly below the mixing line, indicating that although the mantlederived component dominates, the fluid He was diluted by measurable amounts of radiogenic He (R/R_a = 0.02; Sano and Wakita, 1986). Sediment pore-water values are from Sano and Wakita (1986).

the possibility that this is an experimental artifact caused by interlaboratory bias in He isotope measurements cannot yet be discounted.

The ³He/⁴He ratios of the Middle Valley sulfides overlap those recorded for methane-rich submarine vent waters from the southern trough of Guaymas Basin, Gulf of California (7 Ra; Lupton, 1983b). The low value of ³He/⁴He for Guaymas Basin vent fluids may be due to the leaching of ⁴He_{RAD} produced by radiogenic decay of U and Th in the cap of overlying impermeable sediments (Lupton, 1983b), Although it is not known whether the massive sulfide deposit at Site 856 sits atop sediments or basement, drilling at Site 857 nearby revealed 471 m of sediment overlying a sediment-sill complex. The sediment thicknesses are comparable to that at Guaymas Basin and act as an effective barrier to heat loss and fluid upwelling (Davis and Villinger, 1992). The presence of a thick sedimentary cover at both Guaymas Basin and Middle Valley hydrothermal systems suggests that the low ³He/⁴He signature of fluids at both ridge crests may be the result of similar processes, so that comparisons on the basis of He isotopes are justified. More extensive water-rock interaction or longer fluid residence time in the source region may explain the lower ³He/⁴He ratios of vent fluids in Middle Valley and Guaymas Basin.

DISCUSSION

Helium Sources

Fluids venting along the Juan de Fuca Ridge have ³He/⁴He ratios typical of the global mid-ocean ridge system (7.8 to 8.4; Lupton et al., 1989). The low ³He/⁴He ratios in fluid inclusions within Middle Valley sulfides must result from the addition of radiogenic ⁴He to typical MOR vent fluids. Downhole measurements of Hole 856H record a 10-m-thick layer that displays high radioactivity within the sulfide pile (Davis, Mottl, Fisher, et al., 1992). Thus, the hydrothermal fluids have acquired, transported, and deposited significant quantities of radio-elements. Two mechanisms may explain the radiogenic helium component of the Middle Valley hydrothermal fluids: (1) seawater interaction with an aged magmatic system, and (2) sedimentary pore fluids. Both of these potential sources are assessed below.



Figure 2. Ranges of helium isotope compositions of oceanic hydrothermal fluids and basalts, and of deep-sea sediment pore fluids. Middle Valley sulfides ($R/R_a = 5.8$ to 7.1) are more radiogenic than those of typical MOR fluids. Data sources: Loihi seamount (Kodera et al., 1988); mid-ocean ridge basalts (average from Trull et al., 1990); MOR vent fluids (Lupton et al., 1989); Guaymas Basin vent fluids (Lupton, 1983a); 21°N EPR sulfides (Turner and Stuart, 1992); and deep-sea sediment pore fluids (Sano and Wakita, 1986).

Magma Aging

Degassing of MOR magmas is expected to increase the (U + Th)/He ratio of the residual magma. The subsequent decay of U and Th reduces the ³He/⁴He ratio of the remaining volatiles below typical MOR values (Zindler and Hart, 1986). This mechanism may account for low ³He/⁴He ratios (~1 R_a) measured in alkali basalts from seamounts close to the East Pacific Rise at 12°N (Graham et al., 1988).

The tectonic style of the northern Juan de Fuca Ridge is complex and differs from the typical ridge-crest morphology displayed by much of the ridge. Spreading along the northern end of the Juan de Fuca Ridge is accommodated by three en-echelon axial rifts (West, Endeavour, and Middle Valley). This results from the aging of the magmatic system near the anomalously cool Sovanco Transform Fault to the north (Davis, Mottl, Fisher, et al., 1992) and may be important in supplying low ³He/⁴He basalts to the axial rifts of the northern Juan de Fuca Ridge. If the radiogenic helium originates from water-rock interaction in the vicinity of the magma chamber, then the fluid ³He/⁴He reflects the He isotope composition of the source-rock. Source-rock ³He/⁴He decrease through time can be modelled using the conventional decay equations. On short time scales (< 10⁷ yr), the fractional change in ³He/⁴He with time is represented by a factor $f_{3/4}$ given by:

$$f_{3/4} = 1 - [t \times 2.179 \times 10^{-13} \times (U/^{4}\text{He})],$$
 (1)

where t is the age in years, U is the uranium concentration in ppm (and Th/U = 3.5), and ⁴He is measured in cm³ STP/g (Zindler and Hart, 1986). U and Th contents of normal mid-ocean ridge basalts (MORB) are low (0.02 – 0.13 ppm U and 0.03 – 0.4 ppm Th, respectively; Jochum et al., 1983) and generate $0.3 - 2.7 \times 10^{-14}$ cm³STP ⁴He_{RAD}/g/yr. The average U/⁴He ratio of MOR basalts of ~6000 is significantly higher than that proposed for the MORB mantle (630), and indicates that MORB magmas are highly degassed (Zindler and Hart, 1986). To reduce the basalt ³He/⁴He ratio from 8.4 R_a (the typical MORB value; Trull et al., 1990) to 7.1 R_a (the maximum value of Middle Valley sulfides) requires that the hydrothermal fluids interacted with oceanic crust for >130 Ma. For a spreading rate of 6 cm/yr for the Juan de Fuca Ridge the fluid source region is therefore 7800 km



Figure 3. Sulfide R/R_a (open circles) and δ^{34} S (filled circles) variation with depth in Hole 856H. Note that the shallowest sample, with the lowest ³He/⁴He ratio, is not air corrected.

off-ridge, which is clearly unreasonable. Geologic considerations and the position of Middle Valley relative to the Brunhes magnetic Chron indicates that the sediment-covered axial ridge is less than a few hundred thousand yr old (Davis and Villinger, 1992). The low ³He/⁴He ratios measured here therefore cannot be due to the extraction of radiogenic He from ancient basaltic crust.

An alternative may be that the low ³He/⁴He volatiles are extracted from the magma itself. The necessary reduction of magmatic ³He/⁴He ratios occurs when the product $(Ut^4He)t > 4 \times 10^{12}$. If the Middle Valley magmatic system is 300,000 yr old (Davis and Villinger, 1992), the required lowering of magmatic ³He/⁴He ratios will only occur when $(Ut^4He)_{magma} > 1.3 \times 10^7$. Such high U/⁴He ratios are three orders of magnitude higher than that of typical MORB, and are possible in extensively degassed magmas (Zindler and Hart, 1986). This places restrictions on the degree to which magmatic He will be extracted by circulating hydrothermal fluids. The fluids resulting from seawater interaction with a degassed magma will have He/Ne ratios significantly lower than those of fluids venting from presently active spreading ridges. The low He/Ne ratios measured here are consistent with this scenario for Middle Valley, but may merely reflect a significant atmospheric component in the solid samples.

Sedimentary Pore Fluids

The coincidence of abnormally low ³He/⁴He ratios and thick sedimentary sequences in both the Guaymas Basin and Middle Valley hydrothermal systems is circumstantial evidence that the sediments act as a source of ⁴He_{RAD}. In this case, the measured He in the fluids is a mixture of a high ³He/⁴He MOR component (similar to that seen in MOR vent fluids) and a radiogenic component derived from the sediments.

Radio-elements are enriched in ocean-floor sediments by more than 10 times compared to pristine MOR basalts (U = 2.6 ppm and Th = 13.5 ppm; Taylor and McLennan, 1985). In-situ decay of U and Th in deep-sea sediments produces 7×10^{-13} cm³ STP ⁴He_{RAD}/g/yr. He abundances and isotope ratios of ocean floor sediments are variable and are the result of mixing between in-situ radiogenic He and extraterrestrial He from interplanetary dust particles (IDP) (e.g., Takayanagi and Ozima, 1987). Sediments sampled close to continental margins, where sedimentation rates are high, are characterized by radiogenic He (Sano and Wakita, 1986). The thick sequence of turbidites in Middle Valley attests to high sedimentation rates during the Pleistocene and Holocene and implies that sediment ³He/⁴He ratios are low.

If all of the measured Ne is derived from Pacific deep waters, ⁴He_{RAD} concentrations in the trapped hydrothermal fluids are in the range 2.2–3.8 × 10⁻⁷ cm³ STP/cm³. Concentrations of radiogenic He in deep-sea sediments are typically 3×10^{-7} cm³STP/g (Takayanagi and Ozima, 1987). If ⁴He_{RAD} is quantitatively extracted from the sediments by the circulating hydrothermal fluids, then water-sediment ratios must approach unity. It is probable that a proportion of the measured Ne (and He) is not derived from the fluid inclusions but is from some atmospheric contamination, either from adsorbed/ implanted air or from hydrated minerals. Thus, the calculated ⁴He_{RAD} concentrations for Middle Valley must be treated as maxima.

Localized, lateral flow of ~200°C hydrothermal solutions through permeable sedimentary layers that was inferred following drilling of the active hydrothermal system suggests that there may be extensive sediment-fluid interaction in this type of ridge environment. However, the sulfide mineralogy at Middle Valley is identical to that of typical MOR hydrothermal sites (Duckworth et al., this volume). In particular, the Middle Valley sulfides lack enrichments in Pb, As, Sb, etc., that identify significant high-temperature fluid-sediment interaction (Koski et al., 1988). Radiogenic He may have been present before basalt-fluid interaction at depth, if the recharging fluid was partly derived from the overlying turbidite pore waters. The U, Th, and He contents of the sediments beneath the sulfide body at Middle Valley are presently unknown as drilling did not fully penetrate the deposit. Further work is required to determine whether the deep sediments can supply sufficient radiogenic ⁴He to lower MOR ³He/⁴He ratios to those measured in the sulfides.

3 He/ 4 He – δ^{34} S Relationships

The lack of sedimentary layers within the Middle Valley massive sulfide deposit suggests that mineralization occurred directly on the seafloor, rather than at the sediment/basalt interface. If so, the sulfide "stratigraphy" may record the evolution of the hydrothermal fluids with time. Increasing ³He/⁴He ratios with depth (Fig. 3) may imply that water-sediment ratios decreased or fluid residence times increased during mineralization. From the limited number of samples analyzed, no clear trend is evident from Figure 3. It is interesting to note, however, that the lowest ³He/⁴He ratios occur between approximately 60 and 70 mbsf, in a zone that has the highest δ^{34} S values. Unfortunately, the large error on many ³He/⁴He measurements may be partly responsible for obscuring possible subtle trends in these data.

The ³He/⁴He variations in the sulfide fluids from Middle Valley are consistent with mixing variable proportions of a high ³He/⁴He basaltic component with a low 3He/4He radiogenic component derived from the sediment pore waters. Such mixing is commonly invoked to explain variations of ³He/⁴He in hydrothermal fluids from the continental crust (e.g., Kennedy et al., 1985). The 3He/4He ratios of the end-members may be assumed to be constant. Variation in the resultant fluid ³He/⁴He ratios may be generated by mixing different proportions of the end-member fluid components, or changes in the He concentration of the end members varies. Temporal variations to the supply of the fluids might occur as a result of changes in fluid pathways. This may occur in response to fracturing, controlled by seismic/magmatic events, or to blockage by mineral precipitation. He concentrations of MOR vent fluids vary spatially and temporally in response to processes occurring deep within the magmatic system, e.g., boiling (Butterfield et al., 1990) and melt replenishment (Lupton et al., 1989). A decrease in the flux of basalt-derived volatiles is expected as the magmatic system ages, increasing the relative importance of the other helium source-rocks, e.g., the sedimentary pore fluids, and would be reflected in a progressive decrease of 3He/4He through time.

The $\delta^{34}S_{CDT}$ values of the Middle Valley sulfides, analyzed for He, range from +1.6‰ to +8.4‰ (Table 1). Pyrite is the dominant Fe sulfide present; pyrrhotite was analyzed in only two cases. The values

reported here are significantly higher than those for sulfides from typical sediment-free ridge crests. For example, δ^{34} S values of sulfides at 21°N EPR range from +1‰ and +4‰ (Woodruff and Shanks, 1988, and references therein). Values heavier than +4‰ are explained either by the replacement of sulfate by sulfide (Shanks and Seyfried, 1987), or by the entrainment of seawater by the hydrothermal fluids (Woodruff and Shanks, 1988). The sulfate required for the high values measured at Middle Valley may be derived from ambient seawater, seawater-dominated pore fluids in the sediments, or directly from sedimentary sulfate.

Pyrite b34S values are plotted against 3He/4He in Figure 4, along with data from 21°N EPR. No clear relationship between He and S isotopes is evident from the Middle Valley data alone, but they display a broad negative trend when combined with the data from 21°N EPR. ³He/⁴He ratios from the 21°N EPR sulfides are similar to those of MOR vent fluids (7.8 \pm 0.2 R_a) and accompany typical ridge-crest sulfur isotope ratios (+1‰ to +3.5‰; Stuart et al., 1992). The radiogenic helium in the Middle Valley inclusion fluids correlates with high $\delta^{34}S_{\text{pyrite}}$ values, which have been explained as being due to the presence of sedimentary pore fluid sulfur in the evolving hydrothermal stockwork zone (Duckworth et al., this volume). The lack of a close correlation with He indicates that the processes controlling 3He/4He and $\delta^{34}S$ variations are decoupled locally. However, the broad trend implies that both processes operate at Middle Valley and provides strong evidence for the role of sediments in the lowering of 3He/4He ratios of fluids in hydrothermal systems of in sediment-covered ridge crests. Investigations of the trapped fluids at this and other sedimentcovered ridge hydrothermal systems (e.g., Escanaba Trough, Gorda Ridge) is clearly required to assess the validity of this relationship. Such investigations are currently underway.

Heavy Noble Gas Abundances and Absolute He Concentrations

The heavy noble gas abundances of Middle Valley sulfides (data not included herein) are 10 to 50 times higher than those measured in ocean-floor sulfides from 21°N EPR (Turner and Stuart, 1992). This intuitively suggests that a significant contribution of air-derived noble gases are present in the Middle Valley sulfides. Ar and Xe isotope ratios are indistinguishable from the air values. XRD analyses indicate that hydrated minerals such as chlorite, serpentine, and talc are present in all of our samples (Table 1). These are not sedimentary in origin, but formed late in the evolution of the system when vent fluids mixed with seawater during hydrothermal reworking. Hydrated phyllosilicates are known to trap high concentrations of Ar, Kr, and Xe (Podosek et al., 1980) as a result of solution and/or adsorption of atmospheric gases. In a data compilation, Ozima and Podosek (1983) failed to identify any consistent abundance pattern from sedimentary rocks except a general trend of enrichment of heavy noble gases. The difficulty experienced in pumping/cleaning these samples and the high concentrations of Ar, Kr, and Xe suggest that the heavy noble gases are associated with the hydrated minerals. We note that the release of the heavy noble gases by crushing requires that they are only loosely bound to the hydrated minerals.

The results presented here contrast with those obtained for fluid inclusions in sulfides from 21°N EPR (Turner and Stuart, 1992). Turner and Stuart (1992) reported that He/Ar ratios, corrected for the presence of small volumes of air using Kr/Ar ratios, were close to the values measured in the vent fluids. Studies of noble gases in fluid inclusions in pure mineral separates (e.g., Böhlke et al., 1989; Böhlke and Irwin, 1992; Stuart et al., unpubl. data) suggest that, to a first order, Ne-Ar-Kr abundances are consistent with this mixing relationship. This cannot be extended to samples where fine-grained, hydrated minerals are present, however. This rules out the determination of absolute concentrations of helium in the fluids and emphasizes the necessity of careful sample selection in the study noble gases dissolved in fluid inclusions.



Figure 4. R/R_a vs. $\delta^{34}S$ for Middle Valley sulfides. The data overlap those for sulfides from 21°N East Pacific Rise, a typical mid-ocean ridge setting, and display a broad negative correlation that implies that the processes controlling He and S isotope variation in MOR hydrothermal systems are linked. Data for 21°N EPR sulfides are from Stuart et al. (1992).

SUMMARY

Sulfide minerals from Site 856 of ODP Leg 139 precipitated from fluids that are enriched in mantle-derived He. Air-corrected 3 He/ 4 He ratios (5.8 to 7.1 R_a) are lower than typical mid-ocean ridge vent fluids (~8 R_a). This is due to the addition of radiogenic He either during seawater circulation in the aging magmatic system beneath Middle Valley, or from the overlying sediments. In conjunction with data from sediment-free MOR sites, the 3 He/ 4 He and 34 S data suggest a broad negative correlation between He and S isotopes in oceanfloor hydrothermal systems. The isotopically heavy sulfur must originate in the sediments, either from the sedimentary pore fluids or the sedimentary in origin. Unfortunately, 3 He/ 4 He measurements are not sufficiently precise to draw conclusions about the evolution of the hydrothermal system.

ACKNOWLEDGMENTS

As ever we thank Dave Blagburn for his technical expertise (and cheery good humor) in the isotope laboratory. Thanks to Paul Harrop for XRD analyses. John Slack, Mack Kennedy, Andrew Fisher, and an anonymous reviewer provided many comments that have improved this manuscript. Noble gas work at the University of Manchester was funded by NERC.

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Date of initial receipt: 7 December 1992 Date of acceptance: 23 July 1993 Ms 139SR-227