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8. LEAD ISOTOPE COMPOSITIONS OF THE TAG MINERALIZATION, MID-ATLANTIC RIDGE, 26°08′N[1]

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ABSTRACT

Lead isotope analyses were performed on sulfides from the Trans-Atlantic Geotraverse (TAG) hydrothermal site, located at 26°08′N, on the unsedimented, slow-spreading Mid-Atlantic Ridge, which is characterized by a high Pb isotopic heterogeneity of the basalts erupting along its axis. Pb isotope ratios of TAG massive sulfides are very uniform. Reported in Pb-Pb diagrams, TAG sulfide data plot on the Northern Hemisphere Reference Line and define a small domain compared with the larger field of the Mid-Atlantic Ridge basalts, which suggests that the main lead sources for the TAG mineralization are the components of the upper oceanic crust. The means of the Pb isotopic compositions of TAG sulfides and neighboring basalts are similar, and identical to the lead composition of present TAG hydrothermal vent fluid. These data suggest that the Pb isotopic ratios of TAG sulfides reflect the average isotope composition of the upper part of the oceanic crust affected by the large-scale hydrothermal fluid circulation, and that the Pb isotopic compositions of the hydrothermal vent fluids recorded in recent and ancient sulfides remain constant during the active interval of a main hydrothermal vent field such as TAG.

INTRODUCTION

Several active hydrothermal vent fields have been recently discovered along the Mid-Atlantic Ridge (Fig.1): Trans-Atlantic Geotraverse (TAG) at 26°08′N (Rona et al., 1986), Snakepit at 23°22′N (Shipboard Scientific Party, 1986), Broken Spur at 29°10′ N (Murton et al., 1994, 1995) and, near the Azores Triple Junction, Lucky Strike at 37°17′N and Menez Gwen at 37°50′N (Charlou et al., 1995; Fouquet et al., 1995). These discoveries conflicted with the commonly held opinion that slow-spreading ridges are unlikely to be sufficiently energetic to produce extensive submarine hydrothermal systems.

The TAG hydrothermal site has been chosen for a study of Pb isotope systematics on massive sulfides for the following reasons:

1. This site is well known, as it has been the subject of ongoing interdisciplinary studies since the discovery of low-temperature hydrothermal activity and mineralization in 1972–1973 during the Trans-Atlantic Geotraverse project of the National Oceanic and Atmospheric Administration (Rona et al., 1975).
2. It is located on the slow-spreading Mid-Atlantic Ridge, and the geochemistry of Mid-Atlantic Ridge mid-ocean ridge basalt (MORB) is characterized by variations both in isotope and trace element ratios.
3. It is located on an unsedimented spreading ridge. Earlier Pb isotopic studies of sulfides from sedimented mid-ocean ridges show heterogeneous compositions indicative of contributions from Pb of sedimentary and basaltic origin (LeHuray et al., 1988, Fouquet and Marcoux, 1995). The lack of sediment at TAG suggested that less heterogeneous compositions may be encountered.
4. The size of the active hydrothermal sulfide mound is unusual. Based on the recoveries of the 17 holes drilled during Ocean Drilling Program (ODP) Leg 158 (Humphris et al., 1995) estimated that there are about 2.7×10^6 t of massive sulfides above the seafloor and approximately 1.2×10^6 t of sulfides below the seafloor and in the upflow zone ± 0.5 t of sulfate (anhydrite). The TAG mound is estimated to contain ~4×10^6 t of sulfides, similar to that of some ancient ore deposits exploited on the continents. This unusual size suggests the presence of an exceptional hydrothermal circulation in the upper part of the oceanic crust. Therefore, Pb isotopic analyses performed on TAG sulfides would provide a good opportunity to evaluate homogenization processes of the heterogeneous Pb isotopic compositions of the upper oceanic crustal rocks, affected by large-scale hydrothermal circulation.

MAIN GEOLOGICAL CHARACTERISTICS OF THE TAG SULFIDE DEPOSIT: BACKGROUND AND SAMPLE LOCATION

Geologic Background

The TAG hydrothermal vent field is located at 26°08′N, between the Atlantis (33°N) and Kane (24°N) Fracture Zones intersecting the unsedimented slow-spreading Mid-Atlantic Ridge (Fig. 1). The field occupies an area of at least 25 km^2, on the floor and wall of the rift valley east of the axial high. It consists of presently active low and high temperatures zones, as well as a number of relict deposits (Rona et al., 1993a, 1993b). The valley and flank axis of the ridge in the TAG area are deeply incised by normal faults resulting in a relief of about 2000 m from the floor of the broad axial valley to the top of the rift. The hydrothermal deposits and their settings were intensively studied as early as 1972, as a part of the TAG project (Rona et al., 1975). But the active high-temperature mound was discovered in 1985 (Rona et al., 1986; Thompson et al., 1988). According to Rona et al. (1993b), three types of hydrothermal activity were recognized associated with basaltic domes (<1 km in diameter):

1. The present active, large polymetallic sulfide and sulfate mound, 200 m in diameter and 50 m high, with black and white smoker chimneys at the top, is situated off the axis on the floor of the rift valley, at about 2.5 km east of the axis of the Mid-Atlantic Ridge. It lies on an oceanic crust estimated to be 100 ka (Thompson et al., 1988).

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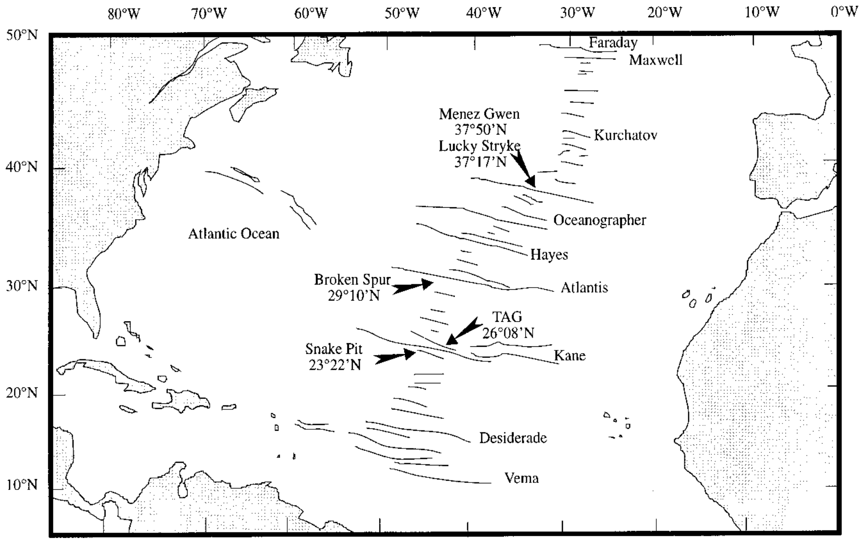

Figure 1. Sketch map of the Mid-Atlantic Ridge between 14° and 50°N with location of the main active hydrothermal vent fields: Snakepit (23°22′N), TAG (26°08′N), Broken Spur (29°10′N), Lucky Strike (37°17′N), and Menez Gwen (37°50′N).

2. On the lower part of the east wall, two large relict zones (*Mir* and *Alvin*) are located at 3 km to the north and 2 km to the northeast of the active mound, respectively.
3. At mid-depth, near the base of the east wall, a low-temperature zone is situated 3.7 km upslope to the east of the active mound.

The large size of the mound and radiometric dating of hydrothermal metalliferous products of the active mound (Lalou et al., 1990, 1993), and the *Alvin* and *Mir* extinct zones (Lalou et al., 1986, 1990, 1993, 1995) suggest that hydrothermal activity has been long lived, multistage, and episodic over the past 100 k.y. The mound high-temperature activity began about 40–50 ka and has been intermittent since then. According to Lalou et al. (1990, 1993), the present-day hydrothermal activity was reactivated only 60 yr ago, after a quiescent period of about 4 k.y.

The aims of this paper are to measure the Pb isotope compositions of TAG sulfides and to compare these with heterogeneous Pb isotopic ratios of Mid-Atlantic Ridge basalts. Thus, two goals were defined: (1) characterization of the lead source of the TAG mineralization, and (2) demonstration of the isotopic homogenization of the lead extracted from the components of the upper oceanic crust during the hydrothermal circulation, and discussion of the significance of the Pb isotope ratios of the TAG sulfides compared to the Pb isotope variations of Mid-Atlantic Ridge basalts in the TAG environment and in the neighboring segments of the ridge.

Sample Location

The circular active mound (Figs. 2, 3) consists of two distinct, flat platforms 130 and 90 m in diameter, respectively; the upper platform is 20 m higher than the lower one. The active fluid discharges are located on these platforms; they appear as shimmering waters and as black smokers and white smokers that emanate from chimneys respectively located at and off center of the mound (Fig. 2). The fluids have a wide range of temperatures, white smokers from 260°C to 300°C and black smokers up to 363°C, and two distinct chemistries (Tivey et al., 1995). The active chimneys are distinct in shape, size, texture, and mineralogy (Thompson et al., 1985, 1988). The black smoker chimneys are predominantly composed of anhydrite and chalcopyrite (Tivey et al., 1995); the mineralogy of the white smoker chimneys is dominated by sphalerite (Tivey et al., 1995).

The Pb isotope analyses were carried out on samples collected from the active mound by the *JOIDES Resolution* during Leg 158 in 1994. Five areas were drilled: on the east and on the south side of the Black Smoker Complex, in the "Kremlin" white smoker area, and finally, on the west and on the north side of the Black Smoker Complex (Fig. 3). Samples recovered by drilling through the active mound, in the vicinity of the white and black smoker vent field, revealed a complex growth history characterized by different stages of cementation, dissolution, and replacement of preexisting products (after Honnorez et al., Chap. 18, this volume). To this new set of samples have been added results of previous studies performed on massive polymetallic sulfide samples recovered during the 1675 and 1676 *Alvin* dives in 1986 (location of *Alvin* samples is shown in Fig. 2). Mineralogical parageneses of all the analyzed samples are reported in Tables 1 and 2.

ANALYTICAL TECHNIQUES

Bulk massive samples were crushed in a stainless steel mortar. The various mineral species were separated using a Frantz Isodynamic Separator. For each analysis, the 4- to 10-mg sulfide fraction were selected by hand-picking under a binocular microscope, and were repeatedly ultrasonically cleaned in 1N HCl and ultrapure water. They were then dissolved in 13N HNO_3 overnight in a Teflon beaker.

After dissolution, samples were evaporated to dryness and the residues were dissolved in 0.5-N HBr. Pb was separated following the anionic exchange microprocedure of Mahnès et al. (1978). Pb separations were performed with 50-µL AG-1X8 200- to 400-mesh anion exchange resin. The elution was carried out with 0.5-N HBr for Fe sulfides and Fe-Cu sulfides, and with 0.1-N HBr for Zn sulfides. Lead was finally eluted with 6-N HCl. The blanks measured were <100 pg. Approximately 200 ng Pb was loaded on a single rhenium filament with silica gel and H_3PO_4 (Cameron et al., 1969). Pb isotopic compositions were determined using a multicollector automatic VG sector mass spectrometer, and were run in static mode. NBS 981 Pb standard was measured before each series of analyses to monitor mass fractionation. Pb isotope data were corrected for mass discrimination by 1.5‰ per a.m.u. Analytical errors (σ) are less than 0.3% for ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb ratios, and less than 0.6% for ^{208}Pb/^{204}Pb ratios.

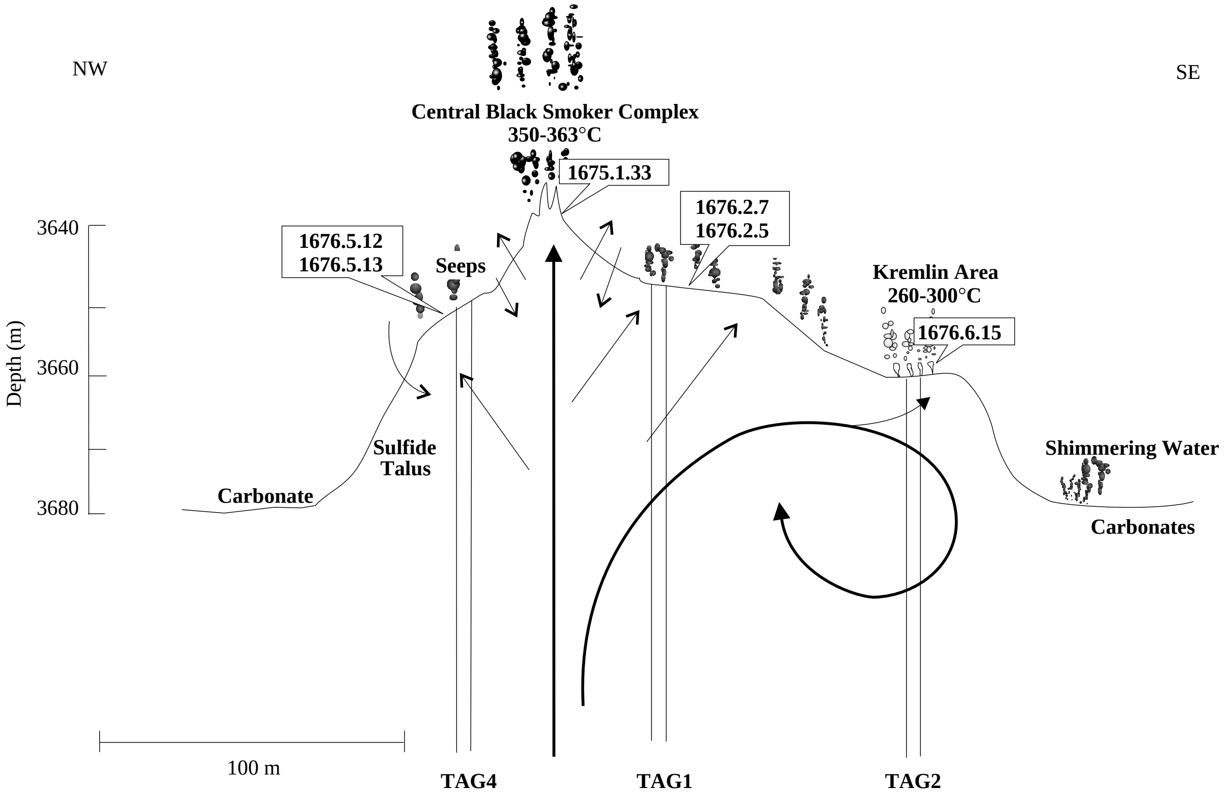

Figure 2. Schematic cross section of the inner active hydrothermal mound of the TAG area with the inferred flow pattern within the mound (after Humphris, Herzig, Miller, et al., 1996), derived from the mineralogy and chemistry of the deposits and the chemistry of white and black smoker fluids (from Tivey et al., 1995). Locations of the analyzed *Alvin* samples and of Leg 158 drill holes are shown. TAG-1 = Holes 957C and 957E–957G; TAG-2 = Holes 957B and 957H; TAG-4 = Holes 957I–957K and 957M.

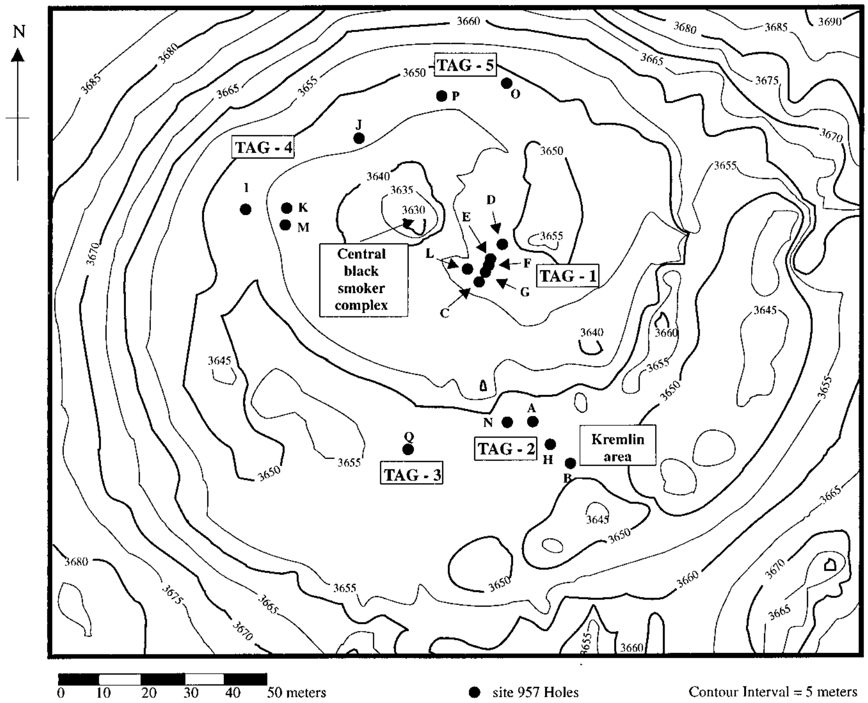

Figure 3. Bathymetric map of the TAG hydrothermal mound (5-m contours). Positions of the five drilled areas and holes are shown (after Humphris et al., 1995).

Table 1. Location and mineralogy of samples from Leg 158.

Hole	Core, section, interval (cm)	Depth (mbsf)	Description*	Mineralization*
TAG-1: East side of the Black Smoker Complex				
957C	7N-2 (Piece 1A, 17-21)	20.83-20.83	Nodular siliceous pyrite anhydrite breccia	50% py - 40% anh - 10% qtz - cpy
957C	12N-2 (Piece 2, 15-17)	35.20-35.27	Massive anhydrite vein	90% anh - 5% py - 5% cpy
957C	15N-1 (Piece 9, 70-74)	42.20-42.73	Siliceous breccia	45% qtz - 40% py - 5% anh - <2% cpy
957G	1N-1 (Piece 4, 18-20)	12.00-12.17	Massive granular pyrite	85-90% py - 5% cpy - 5% qtz - <2% anh
957G	3N-1, (Piece 4B, 40-43)	21.00-21.35	Nodular siliceous pyrite-anhydrite breccia	50% py - 40% anh - 8% qtz - 2% cpy - <2% Fe-oxide
TAG-2: "Kremlin" white smoker				
957H	1N-1 (Piece 3, 6-9)	8.70-8.76	Massive granular pyrite	100% py
957H	3N-1 (Piece 2, 9-12)	17.70-17.78	Massive pyrite breccia	85-95% py - 5-10% anh - 3% cpy
957H	3N-1 (Piece 8, 36-40)	17.70-18.06	Massive pyrite breccia	85-95% py - 5-10% anh - 3% cpy
TAG-4: West side of the Black Smoker Complex				
957I	1N-1 (Piece 10, 63-65)	9.00-9.60	Porous massive pyrite	80% py - 10% cpy - 5% ma - 5% sp - qtz
957K	1X-1 (Piece 5, 38-39)	0.00-0.30	Porous massive pyrite	80% py - 10% qtz - 8% ma - 3% cpy -2% sp
957M	4R-1 (Piece 9, 36-38)	19.30-19.66	Porous massive pyrite	85% py - 5% ma - 5% qtz - 3% cpy - 2% sp
TAG-5: North side of the Black Smoker Complex				
957P	8R-1 (Piece 3, 9-13)	35.10-35.18	Porous massive pyrite	80% py - 15% anh - <2% cpy - <2% qtz
957P	9R-1 (Piece 4, 22-28)	40.10-40.32	Massive granular pyrite	80% py - 15% qtz - 2% anh - 3% cpy
957P	11R-1 (Piece 4, 18-21)	50.10-50.28	Pyrite-silica breccia	70% qtz - 30% py - trace-2% chl - <2% anh - <2% cpy
957P	12R-2 (Piece 10, 54-56)	55.64-56.13	Porous massive pyrite	85% py - 15% anh - <2% cpy - <2% chl - <2% qtz
957P	12R-4 (Piece 9, 75-77)	57.10-57.84	Massive granular pyrite	93% py - 5% qtz - <2% cpy - 2% anh

Notes: * = description according to Humphris, Herzig, Miller, et al. (1996). Mineral abbreviations: py = pyrite, ma = marcasite, po = pyrrhotite, cpy = chalcopyrite, sp = sphalerite, anh = anhydrite, qtz = quartz, chl = chlorite.

Table 2. Petrography and mineralogical association of samples from *Alvin* dives.

Sample number	Location, description, petrography	Mineralogy*
1675.1.33	Active black smoker chimneys cluster, center of the mound. Small finger: concentric layering around an axial conduit; inner zone of chalcopyrite, outer zone of a spongy textured intergrowth of chalcopyrite and Fe sulfides.	Inner lining: massive chalcopyrite, traces of sphalerite. Sulfate between the sulfide phases. Fe sulfides in the matrix.
1676.2.5	Active black smoker chimneys at center of mound. Chimney fragment: numerous channels, with chalcopyrite in inner parts. Matrix of chalcopyrite and Fe sulfides.	Red outer layer: pyrite; minor marcasite, chalcopyrite. Inner yellow crystallized lining: chalcopyrite; trace of pyrite. Inner loose dark matrix: chalcopyrite, minor pyrite, gypsum.
1676.2.7	Active black smoker chimneys at center of mound; base of complex near flow marker. Chimney fragments: "good" outer crust fine-grained unconsolidated intergrowth of Fe sulfides and chalcopyrite.	
1676.5.12	Edge of inner mound, area of shimmering water. Large, relict chimney fragment. Outer red, granular layer. Interior of tubular vents and finger-like protrusions. Two small cores were analyzed: near conduit (1676.5.12.A) in the central part of the sample and Fe sulfides in the outer zone (1676.5.12.B).	Dark red outer layer: marcasite, pyrite; trace chalcopyrite. Inner matrix; trace pyrite, gypsum. Yellow crystallized vent lining: chalcopyrite; traces of pyrite, sphalerite.
1676.5.13	Edge of inner mound, area of shimmering water. Finger-like protrusion, tip of chimney: black matrix of Zn sulfide. In central part of samples well developed inner vents, often with thin membrane-like walls. Two small cores, one in the central part (1676.5.13.A), the second near the rim of the samples (1675.5.13.B).	Around the channel: sphalerite, hydrated Zn sulfates†, chalcopyrite, matrix of sphalerite and hydrated Zn sulfates†.
1676.6.15	Kremlin region, sampled active smoker. Region of white and blue-white smokers, bulbous domes with well-developed crenulate or onion-like morphology on outer surfaces. Complete chimney (broken into three parts: the head, base, and nose): "good" development of crenulate structures near "head" and "nose". The sample analyzed was from the nose (1676.6.15).	Black, interior matrix of colloform sphalerite high porosity, 70% to 80% at least. Trace chalcopyrite in external limits of cavities, small amounts of marcasite and pyrite.

Notes: * = after XRD measurements summarized in *Alvin* samples catalog and studies on polished sections and polished thin sections conducted in collaboration with J. Honnorez and B.M. Honnorez-Guerstein. † = after Lalou et al. (1990).

LEAD-ISOTOPE RESULTS AND DISCUSSION

Pb isotope data of the TAG sulfides are listed in Tables 3 and 4 and plotted on the conventional ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb diagrams (Figs. 4, 5).

Comparison with the North Atlantic MORB Collected Along the 70° to 10°N Latitudes of the Mid-Atlantic Ridge

Pb isotope ratios are commonly used to characterize and identify the origin of polymetallic ore bodies. For recent hydrothermal mineralization located on mid-oceanic ridges, three main potential sources of Pb are usually considered: the components of the upper oceanic crust (i.e., basalts, diabases, and gabbros), the sediments, and seawater.

To compare with TAG sulfide data, fields of these three components are plotted on Pb-Pb diagrams (Fig. 4) where:

1. The broad field for MORB from the North Atlantic Ocean is obtained by compilation of the large number of data available for Mid-Atlantic Ridge basalts erupted between 70° and 10°N (Sun, 1980; Hamelin et al., 1984; Ito et al., 1987; Dosso et al., 1991, 1993);
2. The Atlantic sediment field is defined by Pb isotope ratios of terrigenous, pelagic and biogenic, sediments (Ben Othman et al., 1989); and
3. Pb isotopic ratios of Fe-Mn nodules (Godfrey et al., 1994; Mills et al., 1993; Ben Othman et al., 1989) are plotted on the Pb-Pb diagrams (Fig. 4) to define the Mid-Atlantic Ridge seawater field, because only one sample of Atlantic seawater, collected in the Sargasso Sea, has been analyzed for Pb isotopes

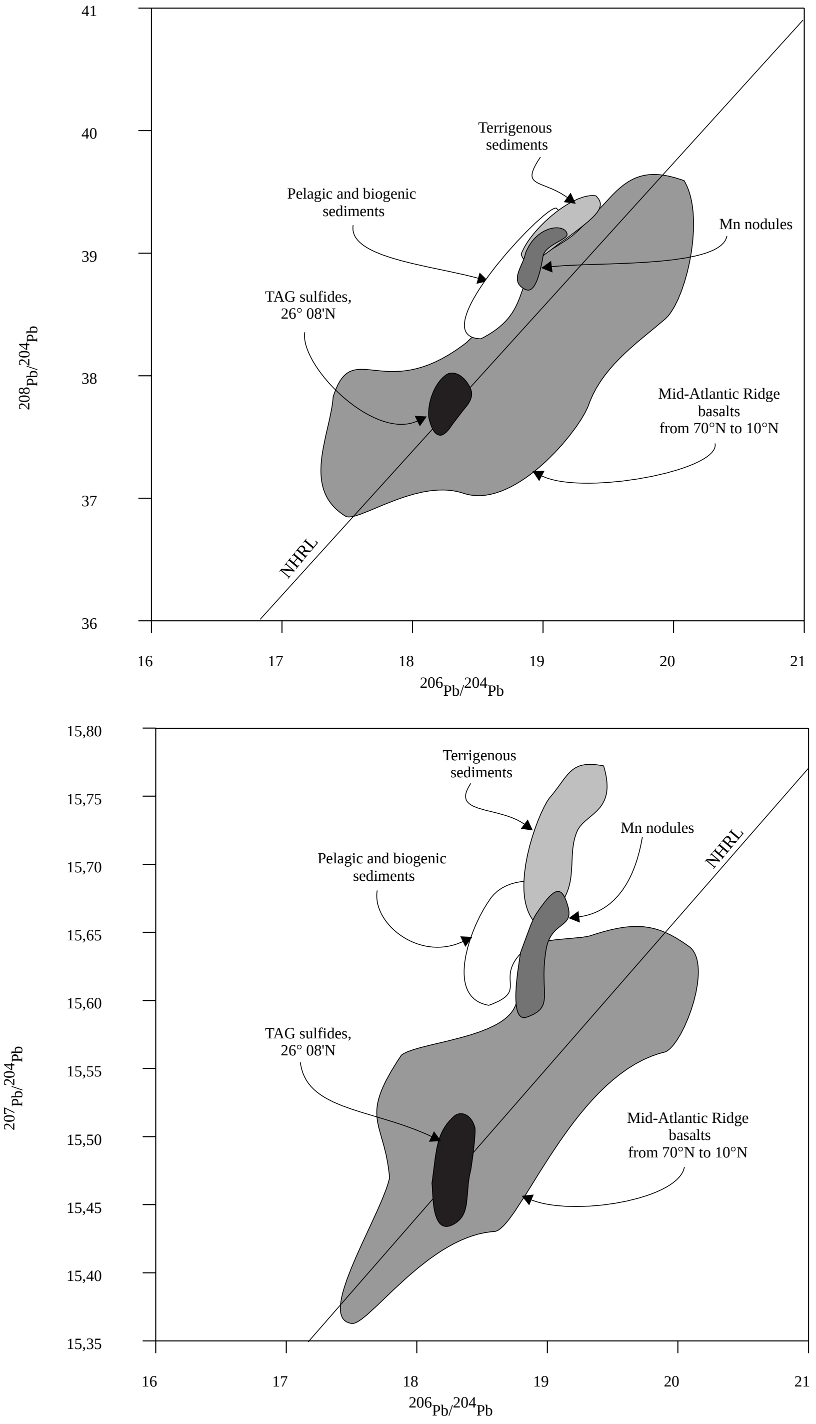

Figure 4. ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (**top**) and ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (**bottom**) diagrams for TAG sulfides and representative domains of the Mid-Atlantic Ridge basalts from 10° to 70°N (Sun, 1980; Hamelin et al., 1984; Ito et al., 1987; Dosso et al., 1991, 1993), Atlantic sediments (Ben Othman et al., 1989), and Mn nodules (Ben Othman et al., 1989; Mills et al., 1993; Godfrey et al., 1994). NHRL = the Northern Hemisphere Reference Line according to Hart (1984).

(Shen and Boyle, 1988). Thus, the Pb isotope composition of seawater is commonly considered to be almost the same as that of Mn nodules.

The Pb isotopic ratios of TAG sulfides are very homogeneous and define a very small domain enclosed within the field of the large Pb data from North Atlantic MORB (Fig. 4). The TAG sulfide domain plots on the Northern Hemisphere Reference Line (NHRL), defined by Hart (1984). Pb isotopic compositions of the TAG sulfides are clearly less radiogenic than those of Atlantic sediments or Mn nodules. These data suggest that the main source for Pb in the TAG mineralization is the upper oceanic crustal rocks.

Following the discovery of the correlation between bathymetry and isotopic variations along mid-oceanic ridge magmas (Schilling, 1973), several studies using geochemical tracers (i.e., isotope as well as trace elements) have been performed on MORB (especially from the Mid-Atlantic Ridge). These studies were carried out in order to identify the source of geochemical anomalies along migrating mid-oceanic ridges and discuss their possible relation with mantle plumes (Sun et al., 1975; White and Schilling, 1978; Sun et al., 1979; Sun 1980; Dupré and Allègre, 1980; Cohen et al., 1980; Le Douaran and Francheteau, 1981; Cohen and O'Nions, 1982; Allègre et al., 1984; Hamelin et al., 1984; Dosso et al., 1991, 1993). Because Pb isotope compositions of MORB are very heterogeneous along the slow-

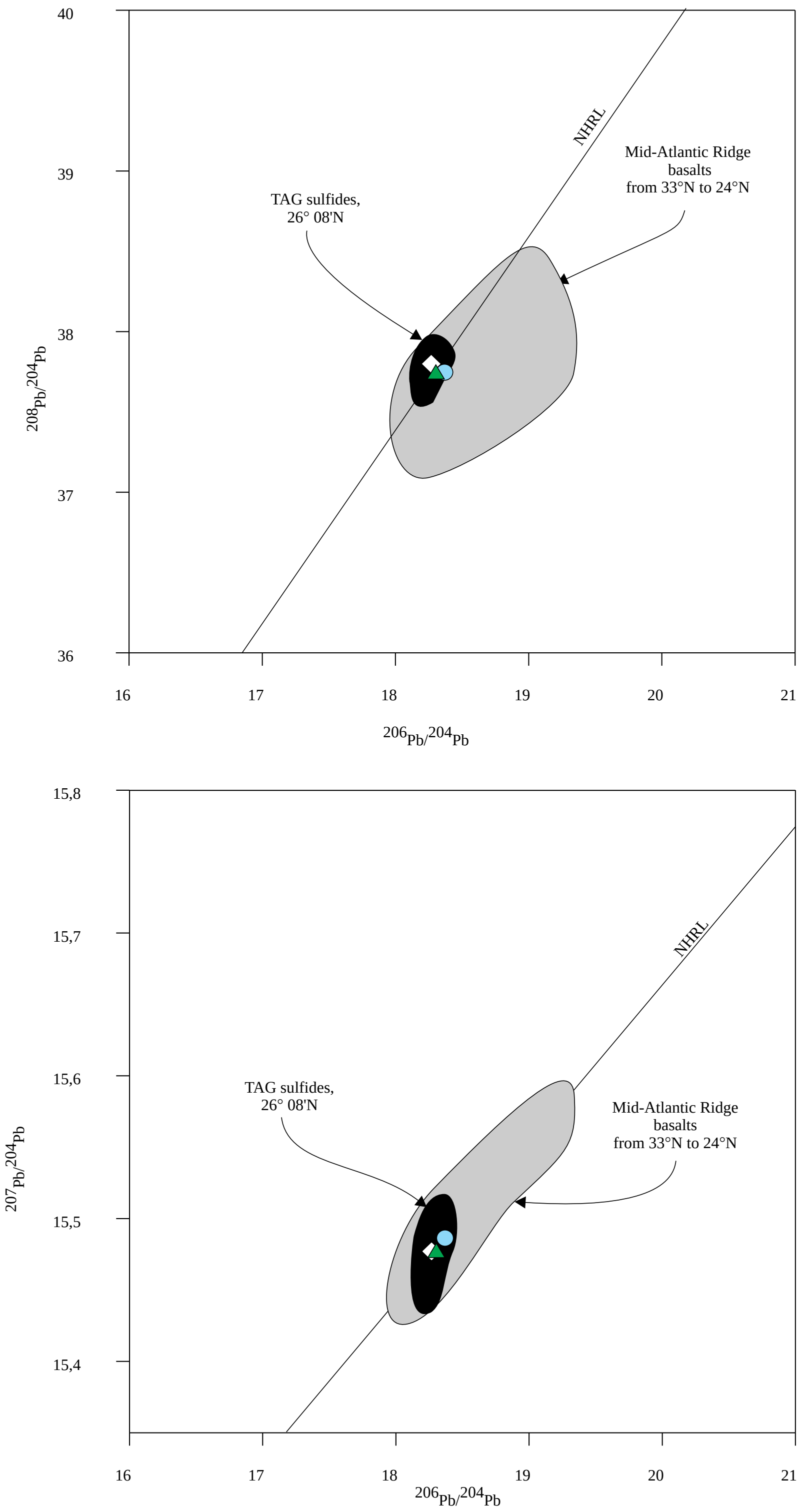

Figure 5. ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (**top**) and ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (**bottom**) diagrams for TAG sulfides and Mid-Atlantic Ridge basalts from 24° to 33°N (Sun, 1980; Hamelin et al., 1984; Ito et al., 1987). Pb isotopic composition of TAG hydrothermal vent fluid (shaded triangle = from Godfrey et al., 1994) and of the means of TAG sulfides (open diamond) and Mid-Atlantic Ridge basalts (shaded circle) from 33° to 24°N are identical within analytical precision. NHRL = the Northern Hemisphere Reference Line according to Hart (1984).

spreading Mid-Atlantic Ridge (Allègre et al., 1984; Hamelin et al., 1984), Pb isotope ratios of TAG massive sulfides should be best compared for the purposes of this study with Pb data from MORB surrounding the TAG field. But no measurements have been performed on basalts erupted in the direct vicinity of the TAG hydrothermal field. Therefore, the basalts collected in the area between the Atlantis (33°N) and Kane (24°N) Fracture Zones where the TAG hydrothermal field lies have been chosen to represent the field for the Mid-Atlantic Ridge basalts surrounding the TAG hydrothermal vent site. The field for Mid-Atlantic Ridge basalts shown in Figure 5 represents the variations observed for samples collected between 33° and 24°N (Sun 1980; Hamelin et al., 1984; Ito et al., 1987).

Comparison with the North Atlantic MORB Collected Along the 33° to 24°N Latitudes of the Mid-Atlantic Ridge

Pb isotope analyses were performed on various sulfide species (i.e., pyrite, chalcopyrite, sphalerite, and pyrite-chalcopyrite association) and on an oxidized crust. The results are listed in Tables 3 and 4.

Table 3. Pb isotope results of Leg 158 sulfide samples from the TAG hydrothermal vent field.

Hole	Core, section, interval (cm)	Depth (mbsf)	Sulfides	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Pb (ppm)
TAG-1							
957C	7N-2 (Piece 1A, 17-21)	20.83-20.83	$CuFeS_2$	18.28	15.483	37.75	
			FeS_2	18.296	15.485	37.846	
957C	12N-2 (Piece 2, 15-17)	35.20-35.27	FeS_2	18.258	15.488	37.775	
957C	15N-1 (Piece 9, 70-74)	42.20-42.73	FeS_2	18.225	15.475	37.769	
957G	1N-1 (Piece 4, 18-20)	12.00-12.17	FeS_2	18.216	15.465	37.761	
			$CuFeS_2$	18.352	15.499	37.888	
957C	3N-1 (Piece 4B, 40-43)	21.00-21.35	FeS_2	18.237	15.48	37.769	
TAG-2							
957H	1N-1 (Piece 3, 6-9)	8.70-8.76	FeS_2	18.212	15.468	37.776	
957H	3N-1 (Piece 2, 9-12)	17.70-17.78	$CuFeS_2$	18.232	15.479	37.809	
			FeS_2	18.235	15.486	37.807	
957H	3N-1 (Piece 8, 36-40)	17.70-18.06	FeS_2	18.256	15.453	37.837	
TAG-4							
957I	1N-1 (Piece 10, 63-65)	9.00-9.60	$CuFeS_2$	18.272	15.486	37.915	
			FeS_2	18.205	15.455	37.715	
			$FeS_2 + CuFeS_2$	18.238	15.485	37.786	
957K	1X-1 (Piece 5, 38-39)	0.00-0.30	$CuFeS_2$	18.202	15.453	37.721	11.16
			FeS_2	18.217	15.468	37.744	172.4
957M	4R-1 (Piece 9, 36-38)	19.30-19.66	$CuFeS_2$	18.224	15.471	37.759	
			FeS_2	18.212	15.46	37.739	
TAG-5							
957P	8R-1 (Piece 3, 9-13)	35.10-35.18	FeS_2	18.31	15.483	37.836	
957P	9R-1 (Piece 4, 22-28)	40.10-40.32	$CuFeS_2$	18.231	15.464	37.774	26.71
			$FeS_2 + CuFeS_2$	18.303	15.484	37.833	
957P	11R-1 (Piece 4, 18-21)	50.10-50.28	FeS_2	18.228	15.48	37.782	
957P	12R-2 (Piece 10, 54-56)	55.64-56.13	FeS_2	18.22	15.466	37.722	
957P	12R-4 (Piece 9, 75-77)	57.10-57.84	FeS_2	18.224	15.4722	37.7793	19.54

Table 4. Pb isotope results on *Alvin* sulfide samples from the TAG hydrothermal mound.

Sample number	Mineral phases	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
1675.1.33	Pyrite	18.314	15.494	37.863
	Chalcopyrite	18.321	15.485	37.855
1676.2.5	Pyrite	18.32	15.487	37.867
	Chalcopyrite	18.365	15.506	37.877
	Oxidized crust	18.296	15.469	37.81
1676.2.7	Pyrite	18.299	15.467	37.78
1676.5.12A	Pyrite	18.308	15.483	37.828
	Chalcopyrite	18.311	15.474	37.81
1676.5.12B	Pyrite	18.317	15.484	37.85
	Chalcopyrite	18.3	15.474	37.797
1676.5.13A	Chalcopyrite	18.277	15.479	37.792
	Sphalerite	18.266	15.48	37.822
1676.5.13B	Sphalerite	18.264	15.464	37.748
1676.6.15	Sphalerite	18.291	15.504	37.854

Pb contents of the four sulfide samples range from 11 to 172 ppm (Table 3), much higher than the usual range of 0.1 to 5 ppm Pb in MORB (Mahnès et al., 1977).

First, a comparison between sulfide samples was made in order to estimate the amplitude of the Pb variations between the different mineral species (Fig. 5). Measured Pb isotopic ratios (Tables 3, 4) show only minor variations, the $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios range, respectively, between 37.692 and 37.915, 15.452 and 15.506, and 18.167 and 18.365, suggesting a common source for the Pb of all the TAG sulfides. These similarities in isotopic compositions among sulfides from various active chimneys (both black and white smoker chimneys) and from massive sulfides from the surface and inner part of the active mound imply that Pb isotope ratios do not correlate with sulfide mineralogy or the chemistry of hydrothermal vent fluids. No change in the Pb isotopic composition of fluids can be observed during successive steps of crystallization of the sulfide paragenesis. In addition, taking into account experimental errors, the calculated averages of Pb isotope ratios for TAG massive sulfides ($^{208}Pb/^{204}Pb = 37.801 \pm 0.099$, $^{207}Pb/^{204}Pb = 15.477 \pm 0.026$ and $^{206}Pb/^{204}Pb = 18.267 \pm 0.089$) are similar to the Pb isotopic composition of a TAG hydrothermal vent fluid ($^{208}Pb/^{204}Pb = 37.770$, $^{207}Pb/^{204}Pb = 15.476$, and $^{206}Pb/^{204}Pb = 18.306$) determined by Godfrey et al. (1994). These data confirm that the Pb of local MORB of the Mid-Atlantic Ridge provide, at least partly, the Pb concentrated in TAG massive sulfides. But, as the fractional crystallization process of basaltic melt, at the origin of diabases and cumulate gabbros, does not change the Pb isotopic composition of the melt, basalts, diabases, and upper part of gabbros of the local oceanic crust constitute the single source of the TAG sulfide Pb.

The mean Pb isotopic compositions of TAG sulfides and basalts from the Mid-Atlantic Ridge segment, where the TAG hydrothermal vent field is located, are also very similar (average $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios for sulfides and basalts are, respectively, 37.801 ± 0.099, 15.477 ± 0.026, and 18.267 ± 0.089, and 37.746 ± 0.531, 15.486 ± 0.074, and 18.368 ± 0.620). These data indicate that the average Pb isotopic composition of the mantle source at the origin of the local oceanic crust can be inferred from the Pb isotopic composition of massive sulfides of the TAG hydrothermal vent field. The isotopically heterogeneous Pb isotopic composition extracted from the upper part of the oceanic crust by the hydrothermal fluid is homogenized during the large-scale hydrothermal circulation, confirming previous studies by Fouquet and Marcoux (1995).

CONCLUSION

Pb isotope systematics were performed on recent TAG hydrothermal massive sulfides from the unsedimented, slow-spreading Mid-Atlantic Ridge. Reported in the Pb-Pb diagrams, Pb isotope compositions of these sulfides plot on the NHRL and within the Mid-Atlantic Ridge MORB domain, but are much more homogeneous than those of the MORB erupted from 70° to 10°N or in the vicinity of the TAG vent field (i.e., from 33° to 24°N).

Furthermore, the various analyzed sulfide species (FeS_2, $CuFeS_2$, ZnS) show the same Pb isotopic composition independent of the mineralogy and the sampling location (black or white active smoker chimneys, outer and inner parts of the mound). Means of Pb ratios calculated for TAG massive sulfides are identical to the Pb composition measured for a TAG hydrothermal vent fluid by Godfrey et al. (1994). Thus, the Pb isotopic compositions of the hydrothermal vent fluids recorded in the TAG massive sulfides do not change with time. In addition, the Pb isotopic compositions of TAG hydrothermal discharges recorded in both sub-recent and recent massive sulfides and defined by the present hydrothermal vent fluids may be compared to the mean of Pb isotopic compositions of 17 MORB samples collected along the Mid-Atlantic Ridge segment (from 33° to 24°N), where the

TAG hydrothermal vent field is located. This comparison suggests that the heterogeneous Pb extracted from the upper part of the slow-spreading ocean crust has been isotopically homogenized within the hydrothermal convective cells. Thus, Pb isotope compositions of TAG massive sulfides contribute to define the main isotopic characteristics of the mantle source affected by the partial melting event at the origin of the local oceanic crust in the vicinity of this hydrothermal vent field.

These data, compared with published Pb isotope sulfide information from sediment-starved ridge sites (Fouquet et al., 1995), confirm (1) the role of basalt as a major source of the lead in this hydrothermal deposit, and (2) the isotopic homogenization of the lead extracted from the components of the upper oceanic crust during hydrothermal circulation.

This study best points out the importance of further systematic lead isotope analyses on massive sulfides from other hydrothermal fields located along the slow spreading Mid-Atlantic Ridge in order to contribute to the definition of the major isotopic variations observed in Mid-Atlantic Ridge basalts.

REFERENCES

Allègre, C.J., Hamelin, B., and Dupre, B., 1984. Statistical analysis of isotopic ratios of MORB: the mantle blob cluster model and the convective regime of the mantle. *Earth Planet. Sci. Lett.*, 71:71–84.

Ben Othman, D., White, W.M., and Patchett, J., 1989. The geochemistry of marine sediments, island arc magma genesis and crust-mantle recycling. *Earth Planet. Sci. Lett.*, 94:1–21.

Cameron, A.E., Smith, D.H., and Walker, R.L., 1969. Mass spectrometry of nanogram-size samples of lead. *Anal. Chem.*, 41:525–526.

Charlou, J.L., Donval, J.P., Fouquet, Y., Costa, I., Lourenco, N., Ondreas, H., Pelle, H., Segonzac, M., and Tivey, M., 1995. DIVA 1 cruise (May 1994): effects of pressure and lave lake proximity on the Lucky Strike and Menez Gwen hydrothermal fluid chemistries. *Terra Abstr.*, 8:206.

Cohen, R.S., Evensen, N.M., Hamilton, P.J., and O'Nions, R.K., 1980. U-Pb, Sm-Nd and Rb-Sr systematics of mid-ocean ridge basalt glasses. *Nature*, 283:149–153.

Cohen, R.S., and O'Nions, R.K., 1982. The lead, neodymium and strontium isotopic structure of ocean ridge basalts. *J. Petrol.*, 23:299–324.

Dosso, L., Bougault, H., and Joron, J.L., 1993. Geochemical morphology of the North Atlantic Ridge, 10°–24°N: trace element-isotope complementarity. *Earth Planet. Sci. Lett.*, 120:443–462.

Dosso, L., Hanan, B.B., Bougault, H., Schilling, J.G., and Joron, J.-L., 1991. Sr-Nd-Pb geochemical morphology between 10° and 17° N on the Mid-Atlantic Ridge: a new MORB isotope signature. *Earth Planet. Sci. Lett.*, 106:29–43.

Dupré, B., and Allègre, C.J., 1980. Pb-Sr-Nd isotopic correlation and the chemistry of the North Atlantic mantle. *Nature*, 286:17–22.

Fouquet, Y., Charlou, J.L., Donval, J.P., Radford-Knoery, J., Pelle, H., Ondreas, H., Segonzac, M., Costa, I., Lourenço, N., and Tivey, M.K., 1995. DIVA 1 cruise. Geological control and composition of hydrothermal deposits near the Azores tripe junction. *Terra Abstr.*, 8:206.

Fouquet, Y., and Marcoux, E., 1995. Lead isotope systematics in Pacific hydrothermal sulfide deposits. *J. Geophys. Res.*, 100:6025–6040.

Godfrey, L.V., Mills, R., Elderfield, H., and Gurvich, E., 1994. Lead behaviour at TAG hydrothermal vent field, 26°N, Mid-Atlantic ridge. *Mar. Chem.*, 46:237–254.

Hamelin, B., Dupré, B., and Allègre, C.J., 1984. Lead-strontium isotopic variations along the East Pacific Rise and the Mid-Atlantic Ridge: a comparative study. *Earth Planet. Sci. Lett.*, 67:340–350.

Hart, S.R., 1984. A large-scale isotope anomaly in the Southern Hemisphere mantle. *Nature*, 309:753–757.

Humphris, S.E., Herzig, P.M., Miller, D.J., Alt, J.C., Becker, K., Brown, D., Brügmann, G., Chiba, H., Fouquet, Y., Gemmell, J.B., Guerin, G., Hannington, M.D., Holm, N.G., Honnorez, J.J., Itturino, G.J., Knott, R., Ludwig, R., Nakamura, K., Petersen, S., Reysenbach, A.-L., Rona, P.A., Smith, S., Sturz, A.A., Tivey, M.K., and Zhao, X., 1995. The internal structure of an active sea-floor massive sulphide deposit. *Nature*, 377:713–716.

Humphris, S.E., Herzig, P.M., Miller, D.J., et al., 1996. *Proc. ODP, Init. Repts.*, 158: College Station, TX (Ocean Drilling Program).

Ito, E., White, W.M., and Göpel, C., 1987. The O, Sr, Nd and Pb isotope geochemistry of MORB. *Chem. Geol.*, 62:157–176.

Lalou, C., Reyss, J.L., Brichet, E., Arnold, M., Thompson, G., Fouquet, Y., and Rona, P.A., 1993. New age data for Mid-Atlantic Ridge hydrothermal sites: TAG and Snakepit geochronology revisited. *J. Geophys. Res.*, 98:9705–9713.

Lalou, C., Reyss, J.,L., Brichet, E., Rona, P. A., and Thompson, G., 1995. Hydrothermal activity on a 10^5-year scale at a slow-spreading ridge, TAG hydrothermal field, Mid-Atlantic ridge 26°N. *J. Geophys. Res.*, 100:17855–17862.

Lalou, C., Thompson, G., Arnold, M., Brichet, E., Druffel, E., and Rona, P.A., 1990. Geochronology of TAG and Snakepit hydrothermal fields, Mid-Atlantic Ridge: witness to a long and complex hydrothermal history. *Earth Planet. Sci. Lett.*, 97:113–128.

Lalou, C., Thompson, G., Rona, P.A., Brichet, E., and Jehanno, C., 1986. Chronology of selected hydrothermal deposits from transatlantic geotraverse "TAG" area, Mid-Atlantic Ridge 26°N. *Geochim. Cosmochim. Acta*, 50:1737–1743.

Le Douaran, S., and Francheteau, J., 1981. Axial depth anomalies from 10° to 50° North along the Mid-Atlantic Ridge: correlation with other mantle properties. *Earth Planet. Sci. Lett.*, 54:29–47.

LeHuray, A.P., Church, S.E., Koski, R.A., and Bousse, R.M., 1988. Pb isotopes in sulfides from mid-ocean ridge hydrothermal sites. *Geology*, 16:362–365.

Mahnès, G., Dupré, B., Hamelin, B., and Allègre, C.J., 1977. Composition isotopique du plomb des roches basaltiques et hétérogeneités du manteau à diverses échelles. *Bull. Soc. Geol. Fr.*,19:1189–1195.

Mahnès, G., Minster, J.F., and Allègre, C.J., 1978. Comparative uranium-thorium-lead and rubidium-strontium study of the Saint Sverin amphoterite: consequences for early solar system chronology. *Earth Planet. Sci. Lett.*, 39:14–24.

Mills, R., Elderfield, H., and Thompson, J., 1993. A dual origin for the hydrothermal component in a metalliferous sediment core from the Mid-Atlantic Ridge. *J. Geophys. Res.*, 98:9671–9681.

Murton, B.J., Klinkhammer, G., Becker, K., Briais, A., Edge, D., Hayward, N., Millard, N., Mitchell, I., Rouse, I., Rudnicki, M., Sayanagi, K., Sloan, H., and Parson, L., 1994. Direct evidence for the distribution and occurrence of hydrothermal activity between 27°N–30°N on the Mid-Atlantic ridge. *Earth Planet. Sci. Lett.*,125:119–128.

Murton, B.J, Van Dover, C., and Southward, E., 1995. Geological setting and ecology of the Broken Spur hydrothermal vent field: 29°10′ N on the Mid-Atlantic Ridge. *In* Parson, L.M., Walker, C., and Dixon D.R. (Eds.), *Hydrothermal Vents and Processes*. Geol. Soc. Spec. Publ. London.

Rona, P.A., Bogdanov, Y.A., Gurvich, E.G., Rimski-Kursakov, A., Sagalevitch, A.M., Hannington, M.D., and Thompson, G., 1993a. Relict hydrothermal zones in the TAG hydrothermal field, Mid-Atlantic Ridge 26°N, 45°W. *J. Geophys. Res.*, 98:9715–9730.

Rona, P.A., Hannington, M.D., Raman, C.V., Thompson, G., Tivey, M.K., Humphris, S.E., Lalou, C., and Petersen, S., 1993b. Active and relict seafloor hydrothermal mineralization at the TAG hydrothermal field, Mid-Atlantic Ridge. *Econ. Geol.*, 88:1987–2013.

Rona, P.A., Klinkhammer, G., Nelson, T.A., Trefry, J.H., and Elderfield, H., 1986. Black smokers, massive sulfides and vent biota on the Mid-Atlantic Ridge. *Nature*, 321:33–37.

Rona, P.A., McGregor, B.A., Betzer, P.R., Bolger, G.W., and Krause, D.C., 1975. Anomalous water temperatures over Mid-Atlantic Ridge Crest at 26°N. *Deep-Sea Res. Part A*, 22:611–618.

Schilling, J.-G., 1973. Iceland mantle plume: geochemical study of Reykjanes Ridge. *Nature*, 242:565–571.

Shen, G.T., and Boyle, E.A., 1988. Thermocline ventilation of anthropogenic lead in the Western North Atlantic. *J. Geophys. Res.*, 93:15715–15732.

Shipboard Scientific Party [ODP Leg 106], 1986. Drilling the Snake Pit hydrothermal deposit on the Mid-Atlantic Ridge. *Geology*, 14:1004–1007.

Sun, S.-S., 1980. Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands and island arcs. *Philos. Trans. R. Soc. London A*, 297:409–445.

Sun, S.-S., Nesbitt, R.W., and Sharaskin, A.Y., 1979. Geochemical characteristics of mid-ocean ridge basalts. *Earth Planet. Sci. Lett.*, 44:119–138.

Sun, S.-S., Tatsumoto, M., and Schilling, J.-G., 1975. Mantle plume mixing along the Reykjanes ridge axis: lead isotope evidence. *Science,* 190:143–147.

Thompson, G., Humphris, S.E., Schroeder, B., Sulanowska, M., and Rona, P.A., 1988. Active vents and massive sulfides at 26°N (TAG) and 23°N (Snakepit) on the Mid-Atlantic Ridge. *Can. Mineral.,* 26:697–711.

Thompson, G., Mottl, M.J., and Rona, P.A., 1985. Morphology, mineralogy, and chemistry of hydrothermal deposits from the TAG area, 26°N Mid-Atlantic Ridge. *Chem. Geol.,* 49:243–257.

Tivey, M.K., Humphris, S.E., Thompson, G., Hannington, M.D., and Rona, P.A., 1995. Deducing patterns of fluid flow and mixing within the TAG active hydrothermal mound using mineralogical and geochemical data. *J. Geophys. Res.,* 100:12527–12555.

White, W.M., and Schilling, J-G., 1978. The nature and origin of geochemical variation in Mid-Atlantic Ridge basalts from the central north Atlantic. *Geochim. Cosmochim. Acta,* 42:1501–1516.

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