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^{230}Th/U DATING OF MASSIVE SULFIDES FROM THE LOGATCHEV AND RAINBOW HYDROTHERMAL FIELDS (MID-ATLANTIC RIDGE)

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Abstract: **A radiochemical study was carried out on massive sulfides from three hydrothermal fields in the Mid-Atlantic Ridge. The main objective was to check whether ^{230}Th/U dating yields reliable results. The absolute ^{230}Th/U ages of massive sulfide samples of three hydrothermal fields at the Mid Atlantic Ridge were determined 58.2±4.2 ka and 16.8±1.0 ka for the "Logatchev-1" site, 3.9±0.4 ka for the "Logatchev-2" site and 23.0±1.5 ka, 3.9±0.6 ka and 2.2±0.3 ka for the "Rainbow" site. The dates correspond to the activation periods of hydrothermal ore formation systems.**

1. INTRODUCTION

Deposits of massive hydrothermal sulfides were discovered in 1978 at 21°N near the axial zone of the East Pacific Rise (Francheteau *et al.*, 1979). Later in 1985 sulfide ores were also found at 26°N of the Mid-Atlantic Ridge (MAR) (Thomson *et al.*, 1985). These discoveries have gathered great scientific and economic interest due to the high concentrations of many metals as Cu, Zn, Au and others. Hence, extended geological and geochronological research on such hydrothermal zones and formations was started.

First numerical dates of sulfides from the MAR were determined by Lalou *et al.* (1986, 1993 and 1996) for the samples from the TAG (26° N), Snake Pit (23° N) and Logatchev-1 (14°45' N) hydrothermal fields. They applied ^{210}Pb/Pb and ^{230}Th/U methods with age limits between 0 and 200 yr and between 2000 and over 250,000 yr, correspondingly. The temporal evolution and duration of hydrothermal activity stages were determined by means of ^{14}C dates of metalliferous sediments from different MAR hydrothermal fields (Metz *et al.*, 1988; Cherkashev, 1995; Bogdanov, 1997 and Gurvich, 1998). But there is still a too small number of dates to get a general view on the frequency and duration of hydrothermal activity stages in the world as a whole and in MAR particularly. Therefore the main objectives of this study were:

- to check whether reliable ^{230}Th/U dates can be determined from oceanic sulfide ores;
- to determine new numerical dates from the Logatchev-1 field and to compare them with those already available for this field;
- to get the first data of numerical ^{230}Th/U ages of massive sulfides from the Logatchev-2 and Rainbow hydrothermal fields.

The samples from the Logatchev-1 and Logatchev-2 fields were collected during the cruises organized by Polar Marine Geosurvey Expedition (PMGE, St. Petersburg) on board R/V "Professor Logatchev". Massive sulfides from the Rainbow hydrothermal field were recovered during the cruise of R/V "Academician M. Keldysh" (Shirshov Institute of Oceanology, SIO RAN, Moscow).

2. GEOLOGICAL SETTING OF THE LOGATCHEV AND RAINBOW HYDROTHERMAL FIELDS

The Logatchev field of hydrothermal activity and sulfide deposits initially was discovered during the cruise of Russian R/V "Professor Logatchev" in 1993-94 at 14°45.2' N, 44°58.8' E, MAR at the 3000 m water depth (Batuyev *et al.*, 1994; **Fig. 1**). It was the first discovery of new type of hydrothermal system associated with not basalts but ultrabasic rocks. Lately, in 1998 three miles SW from the first site another hydrothermal area (Logatchev-2) was found (Cherkashev *et al.*, 2000).

The Rainbow hydrothermal field located at 36°13,8' N, 33°54.3' E (**Fig. 1**) was discovered in 1997 (Fouquet *et al.*, 1998) and was revisited during many other expeditions including the cruise of R/V "Academician M. Keldysh" (Lein *et al.*, 2003).

The Logatchev-1 hydrothermal field is located on the eastern scarp of a rift valley about 55 km south of the Fifteen-Twenty fracture zone. The half-spreading rate of the MAR in this area is 12.8 mm/yr (Fujiwara *et al.*, 2003) indicating that the Logatchev-1 hydrothermal field, which is located 7 km off-axis, is hosted by about 550 ka old oceanic lithosphere. The total area of the field is about 0.3 km^2 and it incorporates 15 hydrothermal mounds. The largest one (called IRINA II) is about 200 m long and up to 100 m wide and has black and white smoker chimneys at its top. Some chimneys are inactive at present. The hydrothermal deposits are overlain by thin discontinuous sediments with debris of gabbroides and serpentinitized ultramafic rocks.

The Logatchev-2 hydrothermal field is located on the same eastern slope of rift valley as Logatchev-1. The field area totals 0.15 km^2 and includes six hydrothermal mounds. The largest one is about 150 m long and up to 80 m wide. The hydrothermal field stretches down-slope from a depth of 2670 to 2740 m. No active smokers are known within this field.

The Rainbow hydrothermal field lies within a protrusion uplift crossing the rift valley floor in a zone of an extensive non-transform offset. The field area totals 0.015 km^2 and includes more than ten active hydrothermal mounds as well as numerous inactive edifices. The hydrothermal field lies at the depth between 2270 and 2320 m.

3. DATING METHODS

Geochronological studies on oceanic sediments are mainly based on the disturbance of the radioactive equilibrium between mother and daughter isotopes of the natural ^{238}U and ^{235}U decay series. Two kinds of dating methods are available:

- the radioactive decay of excess activities for instance of ^{230}Th;
- the growth of the daughter radioisotope from the parent nuclide to radioactive equilibrium.

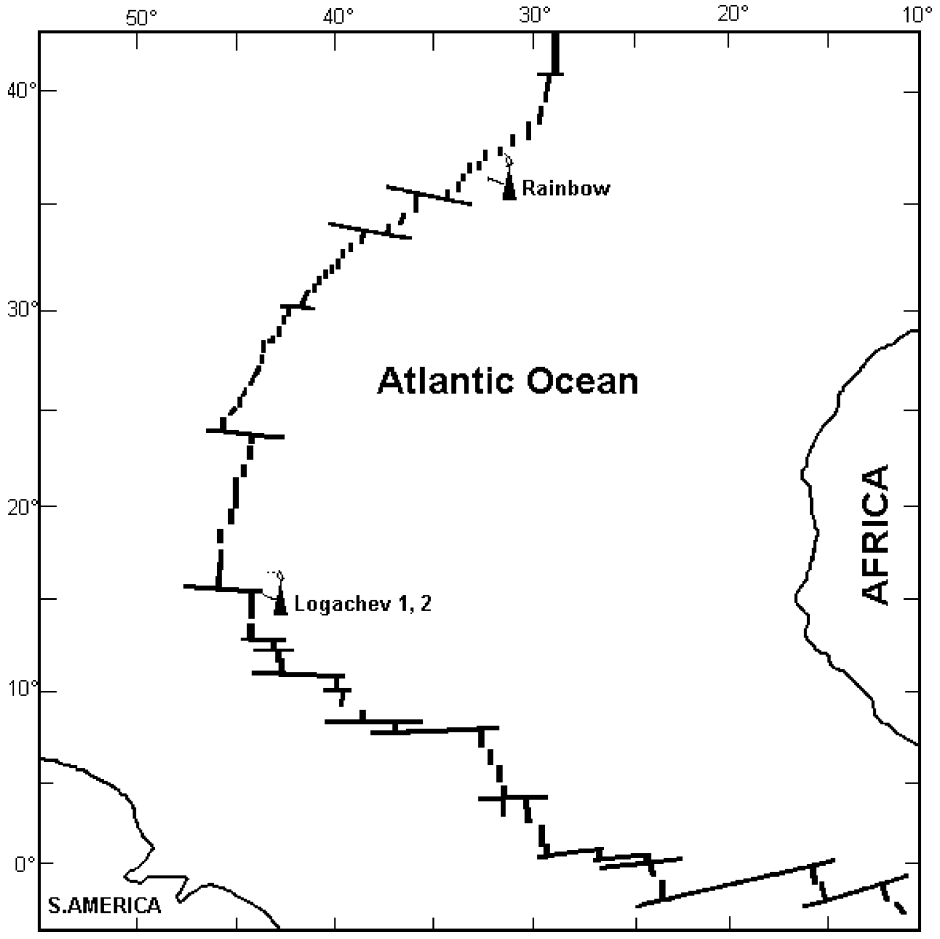

Fig.1. *Scheme of the Mid-Atlantic Ridge and locations of the Logatchev-1, Logatchev-2 and the Rainbow hydrothermal fields.*

The ^{230}Th/U dating method for massive sulfides is an example where ^{230}Th is the decay product of ^{234}U (Ivanovich and Harmon, 1992).

Only the ^{230}Th/U method was used in this study to determine the formation time of sulfides from the Logatchev and Rainbow hydrothermal fields. The sulfides were formed from hydrothermal fluids originated from the seawater circulated in the basalts of the oceanic crust. The reduced hydrothermal fluids contain two orders of magnitude less uranium than the sea water (0.06-0.15 ppb and 3.22 ppb respectively (Chen *et al.*, 1986)). The hydrothermal fluids mix with seawater resulting locally in reducing conditions. By this, easily soluble uranyl-carbonate complexes dissolved in seawater became transformed into easily absorbable uranyl or poorly soluble U^{IV} ions. The latter co-precipitated with transitional sulfides discharged with the fluid. As a result, uranium (without its daughter nuclide ^{230}Th) is accumulated in the precipitated sulfide on the sea floor. Common uranium concentrations here range up to 10 ppm of sample or more (Lalou *et al.*, 1996). ^{234}U later decays to ^{230}Th. Hence, ^{230}Th/U age determinations are based on the present ^{230}Th/^{234}U (and ^{234}U/^{238}U) activity ratios.

There are two main prerequisites for ^{230}Th/U dating of sulfides in oceanic deposits (Lalou and Brichet, 1987; Lalou *et al.*, 1996):

- just deposited sulfides contain uranium but no thorium;
- the sulfides behaved under chemically closed conditions during aging with regard to uranium and thorium.

4. ANALYTICAL METHODS

Uranium and thorium were radiochemically extracted from the sulfide samples (Kuznetsov, 1993; Kuznetsov *et al.*, 2002) with several steps:

- digestion and dissolution of 2-10 g of sulfide in a mixture of concentrated HCl and HNO_3; removal of residue; addition of the ^{232}U and ^{234}Th double spike,
- adsorption of uranium and thorium isotopes on iron hydroxide in a carbonate-free ammonia solution at pH 7 to 8,
- purification of the solution from all admixtures of interfering alpha emitters; separation of the uranium and thorium by anion exchange. Anionite AV-17 was used to elute the Th and U fractions from the 7 n HNO_3 solution by the 8 n HCl and 0.2 n HNO_3 solutions, respectively,
- electro-deposition of uranium and thorium on platinum discs from the ethyl alcohol solution (adding a 0.2 n HNO_3 solution) during 1.5 hours; maintaining a current density of 60 mA/cm^2 (Kim *et al.*, 1966),
- alpha-spectrometric determination of the specific ^{238}U, ^{234}U, ^{232}Th, and ^{230}Th activity using a semi-conductor surface-barrier silicon detector and a pulse analyzer AI-1024.

The chemical yield of uranium and thorium isotopes was calculated from the activities of the ^{232}U and ^{234}Th spikes.

5. RESULTS AND DISCUSSION

Isotopic and hydrochemical results

The results of the radiochemical and chemical analyses of the sulfide samples from the Logatchev-1, Logatchev-2 and the Rainbow hydrothermal fields are compiled in the **Tables 1** and **2**.

Table 1 contains the specific activity of ^{232}Th which is either negligible (samples Log-1a, Log-1b, R-a, R-b, Log-2,) or below the detection limit (samples R-c and R-d). ^{232}Th is bound on suspended mineral matter (containing both isotopes of thorium and uranium) of the seafloor. It is well known that this isotope is a monitor for terrigenic deposits in oceanic sediments (Kuznetsov, 1976). Therefore the low specific activity of ^{232}Th is evidence that terrigenous material is actually absent or at least in the leachate of the samples. It follows that the ^{230}Th is purely radiogenic and formed by decay of its parent radionuclides ^{234}U and ^{238}U of the sulfide deposits. Based on this observation Lalou and Brichet (1982) and Lalou *et al.* (1993 and 1996) confirmed that the first prerequisite for ^{230}Th/U dating of sulfide formations of missing initial ^{230}Th is fulfilled. So, Lalou and Brichet (1982) studied samples of sulfide deposits from the hydrothermal activity zone from the East Pacific Rise.

Table 1. *Results of the radiochemical analysis of sulfide samples from the hydrothermal fields (Mid-Atlantic Ridge).*

No.	^{238}U (ppm)	^{238}U (dpm/g)	^{234}U (dpm/g)	^{234}U/^{238}U	^{232}Th (dpm/g)	^{230}Th (dpm/g)	^{230}Th/^{234}U	Age (ka)
Logatchev-1								
Log-1a	3.89±0.15	2.80±0.11	3.08±0.11	1.10±0.05	0.058±0.009	1.28±0.04	0.415±0.009	58.2±4.4
6/3*	13.01±0.65			1.09±0.02	0.072±0.070		0.42±0.025	58.6±4.6
Log-1b	0.91±0.04	0.66±0.03	0.75±0.03	1.13±0.03	0.001±0.001	0.11±0.01	0.143±0.008	16.8±1.0
9/2*	0.68±0.04			1.16±0.07	<0.004		0.142±0.017	16.5±2.1
Logatchev-2								
Log-2	3.37±0.27	2.43±0.20	2.43±0.20	1.05±0.05	0.001±0.001	0.09±0.01	0.035±0.004	3.9±0.4
Rainbow								
R-a	3.60±0.15	2.59±0.11	2.86±0.12	1.11±0.03	0.054±0.006	0.55±0.02	0.191±0.011	23.0±1.5
R-b	4.75±0.32	3.42±0.23	3.71±0.25	1.08±0.04	0.023±0.003	0.07±0.01	0.020±0.003	2.2±0.3
R-c	0.06±0.01	0.044±0.004	0.050±0.004	1.13±0.14	nd	<0.009	<0.181	<22
R-d	0.24±0.01	0.17±0.01	0.21±0.01	1.21±0.08	nd	0.007±0.001	0.035±0.005	3.9±0.6

** - results obtained by Lalou et al. (1996)*

nd = under detection limit

The ^{210}Pb/Pb age (half-life is about 22 yr) of corresponding samples was < 100 yr and the specific activities of both thorium isotopes were below the detection limit. Inversely, the sulfide samples with age of up to 36.5 ka did not contain ^{210}Pb while the specific ^{230}Th activity was fairly high. ^{232}Th activity was not detected.

The local reducing conditions in hydrothermal activity zones favour the chemical binding of 4-valent uranium in the solid phase of sulfide deposits. Therefore, in active hydrothermal fields with active black smokers at the Logatchev and Rainbow hydrothermal fields prevail reducing conditions which prevent uranium oxidation to mobile 6-valent uranium in the seawater and the formation of soluble uranyl-carbonate complexes. Lalou *et al.* (1996) presumes that the absence of a systematic relationship between the uranium activity and the sample age from the same hydrothermal field gives evidence that closed-system conditions with respect to uranium (preventing addition or leaching) prevailed in the sulfide-sea water system. The uranium distribution within the Rainbow hydrothermal field (**Table 1**) shows that an increase in ^{238}U content from sample R-a to sample R-b leads to a lowering of the age from 23.0±1.5 to 2.2±0.3 ka. On the contrary, lowering of the U concentration in sample R-d increases the age up to 3.9±0.6 ka. Thus, complying with the second requirement of the ^{230}Th/U method (availability of the closed geochemical system in a sample versus uranium and thorium) seems justified and the application of the ^{230}Th/U dating of the sulfide deposits studied may well be justified. Noteworthy, the fact of no thorium isotope migration in different types of oceanic deposits has been proved by many investigations (Kuznetsov, 1976; Kuznetsov and Andreev, 1995), therefore, we believe that there is no reasons for possible migration of thorium (primarily ^{230}Th) in the solid phase of sulfide formations together with pore water.

Thus, the obtained ^{230}Th/U dates show that formation of massive sulfide within Logatchev-1, Logatchev-2 and Rainbow hydrothermal fields took place about 60 ka, 4 ka and 2-4 ka and 23 ka ago, respectively (**Table 1**).

Both our ^{230}Th/U dates of sulfides and those obtained from the Logatchev-1 field (Lalou *et al.*, 1996) agree with each other despite the widely differing specific activities of uranium and thorium (**Table 1**). This gives evidence that the ^{230}Th/U method yields reliable dates of sulfide deposits.

Table 2 compiles the chemical composition of the studied sulfide samples. The concentration of various metals in the ore is very high and changes within a hydrothermal field by several orders of magnitude. This is in agreement with the observed variation of the uranium concentration. These fluctuations may reflect spatial and/or temporal changes of the concentration of the metals in the fluid, differing mixing ratios between fluid and seawater and possibly in relation to stages of hydrothermal activity.

Numerical dating of sulfide ores and the temporal evolution of hydrothermal activity

Metz *et al.* (1988), Cherkashev (1995), Bogdanov (1997) and Gurvich (1998) presented results of chemical analysis and ^{14}C dates of sedimentary cores taken from different hydrothermal fields. These authors determined the layers of metalliferous sediments with a high concentration of iron, manganese and other ore elements. These sediments indicate the events of hydrothermal activity which could have produced massive sulfide deposition. Thus the ^{14}C-dating of the sediments around the hydrothermal fields allows to reconstruct the evolution of hydrothermal systems up to *ca* 50 ka ago (dating limits of the radiocarbon method).

The ^{230}Th/U dating of sulfide samples makes it possible to monitor the oceanic hydrothermal ore formation over at least the last 250 - 400 ka (dating limits of the radiometric and mass spectrometric methods, respectively). Applying of the ^{230}Th dating of sedimentary cores will also extend the time scale up to 250 - 400 ka. We consider that comprehensive studies of sediments and massive sulfides by geochronological (^{210}Pb/Pb, ^{14}C, ^{230}Th/U, ^{230}Th dating) and geochemical methods will give the possibilities to reconstruct the evolution of hydrothermal ore formation during Holocene, Upper and Middle Pleistocene.

6. CONCLUSIONS

A radiochemical study of the massive sulfides from the hydrothermal sites Logatchev-1, Logatchev-2 and Rainbow at the Mid-Atlantic Ridge was carried out. It was concluded that sulfide deposits were formed about 60 ka, 4 ka and 2-4 ka and 23 ka ago respectively and characterized the time of high-temperature hydrothermal activity. The data obtained allowed to apply ^{230}Th/U method to reconstruct the evolution of hydrothermal systems in the

Table 2. *Chemical composition of sulfide samples from the Logatchev-1, Logatchev-2 and the Rainbow hydrothermal fields (Mid-Atlantic Ridge).*

No	Fe (%)	Zn (%)	Cu (%)	Pb (%)	Co (%)	Cd (%)	SiO_2 (%)	CaO (%)	MgO (%)	Al_2O_3 (%)	Ni (ppm)	Au (ppm)	Ag (ppm)
Log-1a	24.33	0.08	35.50	0.020	0.0056	<0.001	nd	0.27	0.52	nd	18	1.24	16.6
Log-1b	17.68	0.36	50.25	0.020	0.0500	0.0013	1.46	0.04	0.06	0.50	140	7.84	18.0
R-c	8.40	51.60	1.30	0.074	0.2000	0.1440	0.44	0.10	0.04	0.30	60	1.00	770.0
R-a	49.70	0.36	15.50	0.006	0.5800	0.0650	0.72	0.10	0.02	0.36	75	4.80	30.0
R-b	47.60	1.72	17.00	0.017	0.5400	0.0100	0.48	0.10	0.04	0.52	120	5.00	40.0
R-d	19.60	36.00	5.20	0.035	0.6600	0.1360	2.60	0.10	0.54	0.04	76	3.70	480.0
Log-2	11.20	38.00	11.60	0.114	0.0400	0.1200	4.20	0.25	0.07	0.38	16	30.00	180.0

nd = under detection limit

ocean. We propose that the most effective way to investigate this problem is to combine geochronological and geochemical studies of both sediments and massive sulfides.

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