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^{230}Th/U CHRONOLOGY OF ORE FORMATION WITHIN THE SEMYENOV HYDROTHERMAL DISTRICT (13°31' N) AT THE MID-ATLANTIC RIDGE

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Abstract: A radiochemical study was carried out on massive sulfides from Semyenov hydrothermal district at the Mid-Atlantic Ridge. New and published results provide evidence that ^{230}Th/U ages obtained for massive sulfides are reliable. The sulfide deposits from the West, North-West, North-East, and East hydrothermal sites at the Semyenov hydrothermal district were formed between ~124 ka and ~37 ka ago. The hydrothermal activity might have started in the eastern part of the district and moved to the west by episodic ore formation.

Keywords: ^{230}Th/U dating, hydrothermal activity, ore formation, massive sulfide, geochronology.

1. INTRODUCTION

The discovery of massive sulfide deposits within the East Pacific Rise and Mid-Atlantic Ridge in the 1970-1980s has gathered great scientific and economic interest due to their high concentration of Cu, Zn, Pb, Fe, Mn, Au, Ag and a number of rare chemical elements as well as their huge size of several tens of millions of tons. Radioisotope dates support the concept of episodic or pulse-type hydrothermal activity and ore-formation (Lalou *et al*., 1995; 1998; You and Bickle, 1998; Kuznetsov *et al*., 2007). The chronology of these hydrothermal activity stages during the last 250 ka can be evaluated applying radiometric ^{230}Th/U dating of sulfide ore deposits. Helpful may be also ^{14}C dating and ^{230}Th dating of metalliferous sediments (Cherkasev, 1995; Kuznetsov, 2008). However, the number of numerical dates is still too small to allow a general view on the frequency and duration of hydrothermal events in the world and particularly within the hydrothermal fields at the Mid-Atlantic Ridge (MAR). Besides, peculiarities of the composition and genesis of hydrothermal deposits require particular studies on the methodical aspects of ^{230}Th/U dating in order to obtain reliable ages of any hydrothermal field.

The main objectives of this study were:

- to check whether reliable ^{230}Th/U dates can be determined from oceanic sulfide ores and
- to determine new numerical dates from the recently discovered Semyenov hydrothermal district at the MAR.

Samples were collected using dredging and a TV-controlled grab system during the cruise on board of R/V "Professor Logatchev" organized by Polar Marine Geosurvey Expedition and VNIIOkeangeologia (St. Petersburg, Russia) in 2007 .

2. LOCATION AND DISTRICT DESCRIPTION

The Semyenov hydrothermal district was discovered during the cruise of Russian R/V "Professor Logatchev"

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in 2007. It is located on the western scarp of a rift valley of the MAR (**Fig. 1**) where the West, North-West, North-East and East hydrothermal fields reside on an underwater mountain. This mountain towers a terrace on 850 m b.s.l. and extends over 10 km in latitudinal direction and about 4.5 km in width (Beltenev *et al*., 2007; 2009).

The West field is located at 13°30’87” N, 44°59’24” W in 2570 and 2620 m b.s.l. The field is about 200 m long and 175 m wide. The hydrothermal activity zones has not yet revealed (Beltenev *et al*., 2007; 2009).

The North-West field is located at 13°31’13” N, 44°59’03” W in a depth between 2360 and 2580 m b.s.l. It consists of two sulfide ore edifices and debris on their base. The first massive sulfide tower has an extension of 600×400 m, the second one 200×175 m. Two zones of modern hydrothermal activity with biocenosis are within the large ore body (Beltenev *et al*., 2007; 2009).

The North-East field is located at 13°30’70” N, 44°55’00” W in a depth between 2300 and 2640 m b.s.l. It has an extension of 1200×650 m. Modern hydrothermal activity was not found (Beltenev *et al*., 2007; 2009).

The East field is located at 13°30’24” N, 44°54’07” W in a depth between 2560 and 3020 m b.s.l. It extends in latitudinal direction approximately 2700 m and in meridian direction approximately 1600 m. Modern hydrothermal activity was not identified (Beltenev *et al*., 2007; 2009).

3. RESULTS AND DISCUSSION

Principal methodical premises of ^{230}Th/U dating of hydrothermal sulfide deposits

The ^{230}Th/U dating method of massive sulfides is based on the disturbance of the radioactive equilibrium between mother and daughter isotopes of the natural ^{238}U decay series in the ocean. The growth of ^{230}Th from ^{234}U by radioactive decay in sulfide ores offers the opportunity to determine their ^{230}Th/U ages by means of the present ^{230}Th/^{234}U and ^{234}U/^{238}U activity ratios (AR).

A thorough check of the applicability of the ^{230}Th/U method is necessary in order to obtain reliable ^{230}Th/U ages of hydrothermal deposits.

There are two main prerequisites for ^{230}Th/U dating of oceanic sulfides ores (Lalou and Brichet, 1987; Lalou *et al*., 1996; Kuznetsov *et al*., 2002, 2006; Kuznetsov, 2008):

1) Sulfides contain uranium without thorium immediately after deposition.
2) Sulfides have behaved under chemically closed conditions with regard to uranium and thorium during aging.

Isotopic results

We carried out radiochemical studies on ore formations from the East Pacific Rise (EPR) and MAR to check these two prerequisites of the ^{230}Th/U dating method.

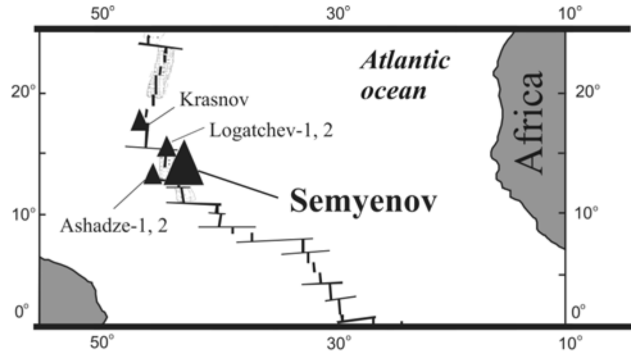

Fig. 1. *Location of the Semyenov hydrothermal district at the Mid-Atlantic Ridge.*

Uranium and thorium were radiochemically extracted from the sulfide samples applying the procedure described earlier by Kuznetsov *et al*. (2002, 2006) and Kuznetsov (2008).

The α-activity of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th was measured with a semi-conductor surface-barrier silicon detector and the pulse analyzer AI-1024. Chemical yields of uranium and thorium isotopes were calculated from the specific activities of the ^{232}U and ^{234}Th spikes. The counting efficiency for uranium and thorium isotopes was checked with a transuranium (^{239}Pu and ^{241}Am) standard of known activity. The results are compiled in **Table 1**.

Check of the two main prerequisites of the ^{230}Th/U dating method of sulfide ores

1) The results show that the specific ^{232}Th activity is very small or below the detection limit. Most ^{232}Th in the ocean is present in suspended terrestrial mineral particles being a tracer of terrestrial material on the sea-floor (Kuznetsov, 1976; Ivanovich and Harmon, 1992). Therefore our samples did contain very little or no terrestrial matter containing ^{238}U, ^{234}U, ^{232}Th, ^{230}Th at least in the leachate of the samples. Hence, most of the ^{230}Th in the samples is radiogenic and formed by radioactive decay of its parent radionuclide ^{234}U in the sulfide deposits.

It is known (Bogdanov *et al*., 2006) that the small-sized edifices in the area at 9°50’ N (EPR) have formed during the last years after the volcanic event in 1991. Radiochemical analyses determined the specific activities of ^{230}Th, ^{232}Th, ^{234}U and ^{238}U in the samples of the active chimney and diffuser (**Table 2**). The specific activity of both thorium isotopes was below the detection limit whereas those of both uranium isotopes were in the range of 0.17-0.74 dpm/g.

Lalou and Brichet (1982) and Lalou *et al*. (1993; 1996) describe similar results. They studied samples of sulfide deposits from the hydrothermal activity zone at EPR. The ^{210}Pb/Pb age (half-life is 22.3 yr) of samples was <100 yr and the specific activities of both thorium isotopes were below the detection limit. In contrast, other

Table 1. *Results of the radiochemical analyses and ^{230}Th/U ages (both 1 sigma) of the sulfide samples from the Semenov Node (MAR).*

№	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{232}Th dpm/g	^{230}Th/^{234}U	^{234}U/^{238}U	Age (±σ), kyr
				The West field			
311-T-1	0.427±0.046	0.409±0.046	0.119±0.008	≤0.015	0.291±0.039	0.957±0.144	$37.4\pm^{6.7}/_{6.1}$
297-M-2	2.885±0.079	3.252±0.086	0.563±0.026	b.d.l.	0.173±0.009	1.127±0.032	20.5±1.3
326-M-1	5.031±0.131	5.560±0.142	0.626±0.027	≤0.018	0.113±0.006	1.105±0.026	12.9±0.8
292	2.328±0.103	2.665±0.111	0.483±0.028	b.d.l.	0.181±0.013	1.145±0.064	21.6±1.7
292-a	4.390±0.205	5.451±0.234	1.477±0.054	b.d.l.	0.271±0.015	1.242±0.069	$33.9\pm^{2.4}/_{2.3}$
292-Б-4	0.311±0.024	0.463±0.030	0.104±0.011	b.d.l.	0.225±0.027	1.488±0.145	$27.3\pm^{3.9}/_{3.7}$
292-Б-1	5.596±0.175	6.286±0.192	1.607±0.046	b.d.l.	0.256±0.011	1.123±0.030	$31.8\pm^{1.7}/_{1.5}$
				The North-West field			
325-T-1	1.089±0.068	1.132±0.070	0.032±0.004	≤0.011	0.028±0.004	1.040±0.078	3.1±0.4
293-T-1	0.074±0.010	0.099±0.012	0.051±0.008	b.d.l.	0.515±0.100	1.327±0.234	$75.8\pm^{25.2}/_{19.7}$
294-T-1	0.893±0.045	0.973±0.047	0.199±0.011	≤0.015	0.204±0.015	1.090±0.066	24.7±2.1
277-T-3/1	0.368±0.029	0.388±0.029	0.108±0.012	≤0.031	0.279±0.036	1.054±0.109	$35.4\pm^{5.8}/_{5.5}$
287-T-1	4.263±0.188	4.778±0.202	1.278±0.055	b.d.l.	0.268±0.016	1.121±0.060	33.6±2.5
287-M-1	0.276±0.015	0.350±0.017	0.068±0.011	b.d.l.	0.195±0.031	1.269±0.089	$23.4\pm^{4.3}/_{4.1}$
287-M-1	0.225±0.026	0.252±0.028	0.045±0.005	b.d.l.	0.180±0.029	1.117±0.175	$21.4\pm^{4.0}/_{3.8}$
				The North-East field			
374-M-1/1	11.98±0.21	12.13±0.21	12.30±0.12		1.014±0.020	1.013±0.011	-
284-Б-1st	0.760±0.046	0.905±0.052	0.345±0.017	b.d.l.	0.381±0.028	1.190±0.088	$51.3\pm^{5.3}/_{5.0}$
284-B-1m	0.499±0.020	0.560±0.022	0.157±0.006	b.d.l.	0.281±0.016	1.123±0.057	$35.5\pm^{2.5}/_{2.4}$
284-B-5a	0.770±0.038	0.961±0.044	0.344±0.018	b.d.l.	0.358±0.025	1.247±0.075	47.3±4.3
284-B-4	1.354±0.064	1.522±0.069	0.871±0.033	b.d.l.	0.572±0.034	1.125±0.062	$90.3\pm^{9.7}/_{8.6}$
				The East field			
353-T-1a	2.367±0.067	2.598±0.072	0.970±0.040	≤0.024	0.373±0.018	1.097±0.032	50.3±3.2
353-M-4a	1.446±0.069	1.568±0.072	0.240±0.010	0.015±0.004	0.153±0.010	1.084±0.059	18.0±1.3
353-M-4/1a	0.708±0.031	0.830±0.034	0.207±0.008	0.011±0.003	0.249±0.014	1.173±0.063	30.8±2.1
354-M-1/2	3.098±0.146	3.673±0.166	2.464±0.054	b.d.l.	0.671±0.034	1.186±0.053	$115.7\pm^{12}/_{10.5}$
354-M-1	3.053±0.090	3.359±0.095	1.330±0.030	b.d.l.	0.396±0.014	1.100±0.032	$54.2\pm^{2.7}/_{2.5}$
354-M-2/4	7.038±0.251	7.518±0.265	3.392±0.069	b.d.l.	0.451±0.018	1.068±0.028	64.6±3.7
354-M-2/5	3.502±0.114	3.838±0.122	2.647±0.044	b.d.l.	0.690±0.025	1.096±0.033	$123.8\pm^{9.7}/_{8.7}$
354-M-3/1	1.347±0.052	1.589±0.058	0.783±0.025	b.d.l.	0.493±0.024	1.179±0.051	$72.2\pm^{5.4}/_{5.1}$
358-M-1a	2.731±0.099	3.166±0.110	0.426±0.020	b.d.l.	0.135±0.008	1.159±0.042	15.7±1.0
359-M-1/1	0.423±0.060	0.545±0.063	0.100±0.013	b.d.l.	0.183±0.032	1.287±0.220	$21.8\pm^{4.4}/_{4.2}$
359-M-3/2	0.568±0.030	0.629±0.032	0.040±0.008	b.d.l.	0.064±0.012	1.108±0.075	7.2±1.4
363-T-1	5.783±0.185	6.666±0.208	0.232±0.015	b.d.l.	0.035±0.002	1.153±0.030	3.9±0.2
363-БС-3	4.766±0.161	5.393±0.178	0.087±0.017	b.d.l.	0.016±0.003	1.131±0.032	1.7±0.4
365-M-1	0.787±0.037	0.923±0.041	0.485±0.023	b.d.l.	0.525±0.034	1.173±0.067	$79.0\pm^{8.3}/_{7.6}$
367-M-4	3.118±0.086	3.665±0.097	0.074±0.005	b.d.l.	0.020±0.001	1.176±0.031	2.2±0.1
145-M-1	0.465±0.027	0.532±0.029	0.150±0.008	b.d.l.	0.283±0.020	1.143±0.082	$35.8\pm^{3.3}/_{3.2}$
153-П-2	0.544±0.024	0.582±0.025	0.101±0.009	b.d.l.	0.174±0.017	1.070±0.062	20.7±2.2
153-П-5/1	0.203±0.015	0.253±0.016	0.071±0.011	b.d.l.	0.280±0.047	1.249±0.119	$35.2\pm^{7.3}/_{6.9}$
145-M-1	0.312±0.024	0.357±0.025	0.083±0.007	b.d.l.	0.233±0.025	1.142±0.114	28.7±3.6

b.d.l. – below detection limit

Table 2. *Specific activities of U and Th in young sulfide samples from the 9°50' N hydrothermal field (EPR) formed after 1991.*

№	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{232}Th dpm/g	^{230}Th/^{234}U	^{234}U/^{238}U	Age year
4668-1	0.172±0.003	0.207±0.003	≤0.0028	b.d.l.	≤0. 0133	1.204±0.018	≤1450
4669/2-1P	0.700±0.016	0.741±0.017	≤0.0027	b.d.l.	≤0. 0036	1.058±0.020	≤390
4668/3	0.473±0.009	0.538±0.010	≤0.0031	b.d.l.	≤0. 0058	1.137±0.019	≤630
4668/6-IBV	0.205±0.007	0.233±0.007	≤0.0041	b.d.l.	≤0. 0174	1.134±0.042	≤1900

sulfide samples with an age of up to several tens of thousands of years did not contain ^{210}Pb while the specific ^{230}Th activity was fairly high. ^{232}Th activity was not detected.

Thus, our and published results provide evidence that the ^{230}Th is purely radiogenic and the first prerequisite for the application of the $^{230}Th/U$ dating method is fulfilled.

2) Lalou *et al*. (1996) presume that a missing relationship between the uranium activity and the sample age from samples collected in the same hydrothermal field provides evidence of closed-system conditions with respect to U (excluding addition or leaching of U) in the sulfide-sea water system. Our data shows that an increase or decrease of the specific uranium activity does not influence the $^{230}Th/U$ age of the samples. **Fig. 2** provides evidence for this statement.

Besides, both $^{230}Th/U$ dates of newly dated sulfides and those obtained from the Logatchev-1 hydrothermal field at the MAR (Kuznetsov *et al*., 2006; Lalou *et al*., 1996) agree with each other despite of widely differing specific activities of uranium and thorium.

Lack of thorium (primarily ^{230}Th) migration in various types of oceanic sediments particularly in the solid phase of sulfide deposits is demonstrated by many investigations (Kuznetsov, 1976; Kuznetsov and Andreev, 1995; Huh and Ku, 1984; Lalou *et al*., 1988). By this, also the second requirement for the $^{230}Th/U$ method seems to be sufficiently substantiated.

$^{230}Th/U$ Age of sulfide ores and the temporal evolution of hydrothermal activity

Our dating results of massive sulfide samples (**Table 1**) deliver as total formation period of ~124 ka. The hydrothermal activity seems to have started at ~124, ~90, ~76 and ~37 ka ago from the East, North-East, North-West to the West hydrothermal fields, respectively **(Fig. 3**). Our dating results of sulfide ore samples support the concept that process of ore formation has had a pulse pattern marked by the certain number of episodes (with duration of up to some thousand years) peculiarly to the studied four fields at the Semyenov district. However, we cannot narrow down precisely the hydrothermal periods due to the small number of ages.

4. CONCLUSIONS

A radiochemical study of the massive sulfides from the West, North-West, North-East and West hydrothermal fields within the Semyenov hydrothermal district at the Mid-Atlantic Ridge was carried out. Our experimental results and published data provide evidence that $^{230}Th/U$ dating yield reliable dates of the formation of hydrothermal deposits. Sulfide deposition in these fields started in the East of the district about 124 ka ago and continued to expand to the West by episodic ore formation.

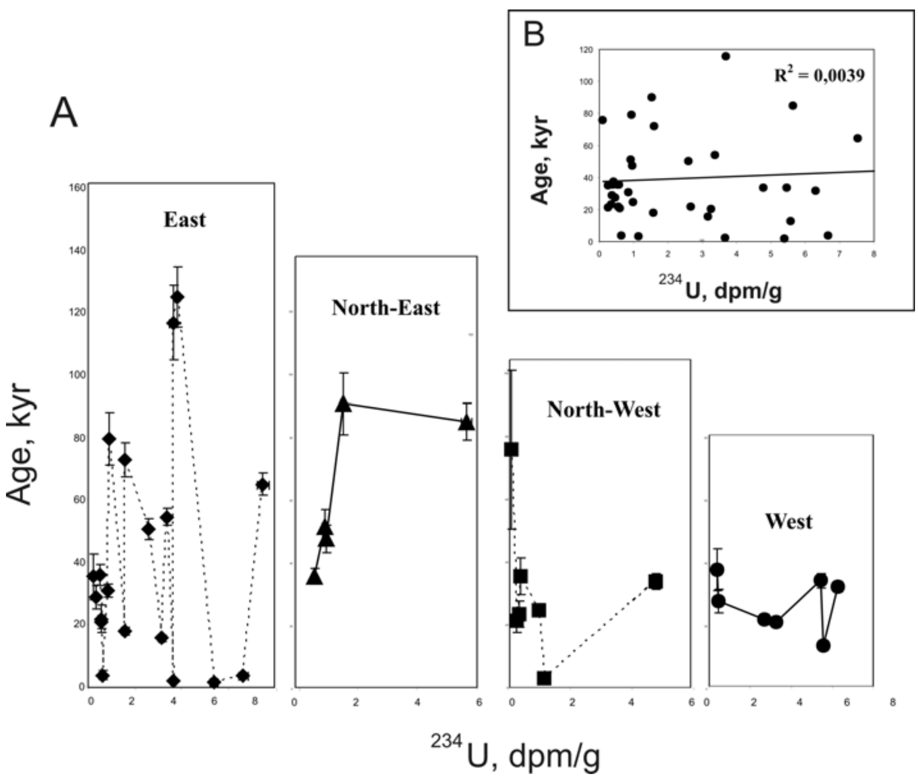

Fig. 2. *$^{230}Th/U$ age vs ^{234}U specific activity for ore samples of the studied hydrothermal fields (A) and the Semyenov district as a whole (B).*

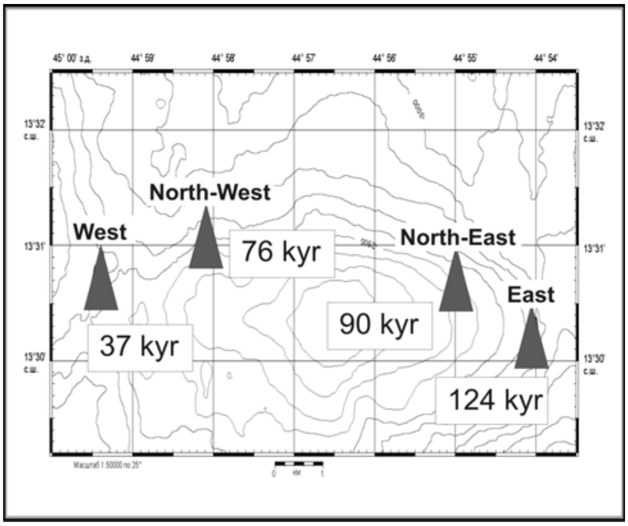

Fig. 3. *230Th/U dates of the initial stages of hydrothermal activity in the Semyenov district (position of the sites from Beltenev* et al.*, 2009).*

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