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THE OLDEST SEAFLOOR MASSIVE SULFIDE DEPOSITS AT THE MID-ATLANTIC RIDGE: ^{230}Th/U CHRONOLOGY AND COMPOSITION

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Abstract: A geochronological and geochemical study on 10 samples of seafloor massive sulfides (SMS) from the inactive Peterburgskoye hydrothermal field at the Mid-Atlantic Ridge (MAR) was carried out. The ^{230}Th/U ages of the SMS are the oldest for the Quaternary hydrothermal ores ever found at the ocean floor. According to them the hydrothermal activity at Peterburgskoye field started at least 170 ka and continued down to 63 ka. The oldest hydrothermal ores from this field consist mainly of pyrite and chalcopyrite and have geochemical properties typical for SMS associated with basalts.

Keywords: Mid-Atlantic Ridge, age of hydrothermal activity, ore formation, ^{230}Th/U dating, geochronology, geochemistry.

1. INTRODUCTION

The ^{230}Th/U method is most widely applied for dating of SMS deposits which formed over a wide age range (from 1–2 ka to about 350 ka). However, only 15 out of 167 hydrothermal deposit sites all over the world were dated by the ^{230}Th/U method (Hannington *et al.*, 2011). For relatively young sulfides the ^{210}Pb and the ^{226}Ra/Ba methods are suited (Finkel, 1980; Lalou *et al.*, 1986; Jamieson, 2013).

The first ^{230}Th/U ages of SMS deposits were determined from the East Pacific Rise (EPR) and the Mid-Atlantic Ridge (Lalou and Brichet, 1982, Lalou *et al.*, 1986, 1988). Later, SMS deposits were dated from the Central Indian Ridge (Münch *et al.*, 2001; Wang *et al.*, 2012). Kuznetsov *et al.* (2006, 2011, 2013) determined ^{230}Th/U ages of sulfides from the Logatchev, Ashadze, Semyenov, Krasnov, Zenith-Victory and Irinovskoye fields located within the Russian exploration area at the MAR (between 12°48'N and 20°54'N). In general, the hydrothermal activity and SMS deposits formation have an age range from 140 ka to the present and occurred in steps.

Recently Shilov *et al.* (2012) and Cherkashev *et al.* (2013) obtained ^{230}Th/U ages of sulfides from the Peterburgskoye hydrothermal field at the MAR discovered during the cruise 33 of R/V "Professor Logatchev" at 19°52'N, 45°52'W in 2010. Six SMS mounds (No. I–VI) were revealed within this field (Shilov *et al.*, 2012). Unexpectedly, an old age of 176^{+59}_{-36} ka was determined for one sample studied. The small precision of this date was due to the low U and Th specific activities. Therefore, a complementary geochronological study of SMS deposits from this hydrothermal field was done.

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Several SMS samples were collected at the newly discovered mound VII of the Peterburgskoye field during the cruise 34 of the Research Vessel (R/V) "Professor Logatchev" in 2011. This paper presents their ^{230}Th/U ages along with geochemical results which clarify the temporal development of the hydrothermal field and the chemical composition of these sulfides.

2. GEOLOGICAL SETTING AND FIELD DESCRIPTION

The Peterburgskoye hydrothermal field has a depth between 2800 and 3100 m and is situated 16 km west of the rift axis (**Fig. 1**). It has the largest distance among all other hydrothermal fields from the rift axis of the MAR. The geological and field description is given in publications by Shilov *et al.* (2012) and Cherkashev *et al.* (2013).

The hydrothermal field extends over 1400×800 m and is surrounded by metalliferous sediments. Basalts subjected to intense hydrothermal alteration are the host of the sulfides. The hydrothermal field consists of six sulfide mounds/ore bodies with extensions of 100×150 m (I), 100×280 m (II), 50×100 m (III), 110×130 m (IV), 50×120 m (V), and 130×180 m (VI) (**Fig. 2**). The recently discovered sulfide mound VII partly overlain by sediments is located 200 m northeast of the first mound and has a size of 150×200 m. The mass of the SMS is estimated to be 2.9 million tons (Cherkashev *et al.*, 2013). Hydrothermal deposits consist of high temperature massive sulfides, sulfide bearing rock breccias and sulfide crusts, as well as precipitates with metalliferous sediments of maximum 40 cm thickness formed at low temperature. Massive sulfides are partially oxidized and are mainly composed of chalcopyrite, covellite, pyrite, marcasite and Fe-oxides. The SMS are usually massif-porous, concentrically-zoned and layered. The texture of sulfides is fine-grained with a relict aphanitic structure of marcasite framework. Diffuser/beehive-like structures were mostly ascribed to the ore body VII.

3. MATERIALS AND ANALYTICAL METHODS

Sample description

Four mounds were sampled. ^{230}Th/U dating was done on ten specimens from mounds II (four samples), V (one sample), VI (four samples) and VII (one sample) consisting of massive sulfide (eight), breccias (one) and a sulfide crust (one) (**Table 1**). The samples contained both primary (high temperature) and secondary (relatively low temperature) minerals such as covellite, atacamite and hematite. The highest content of these minerals had the sulfide crust 33L-41K-2; a high content of opal-like quartz had sample 34L-95M.

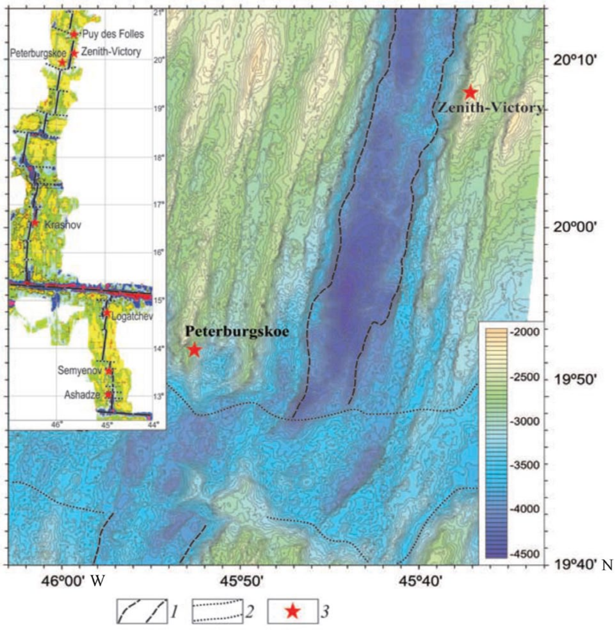

Fig. 1. *Bathymetry with structural elements and SMS deposits (Shilov* et al.*, 2012). Inset map shows SMS distribution along the 12°50'–20°10'N segment of the MAR. 1 — rift valley floor; 2 — non-transform discontinuity; 3 — SMS deposits.*

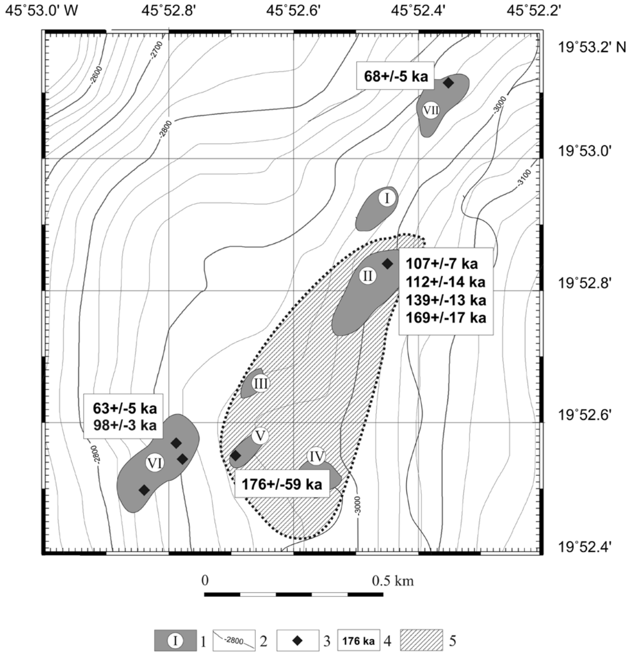

Fig. 2. *Sketch map of the Peterburgskoye hydrothermal field (modified after Shilov* et al. *(2012)). 1 — SMS mound and its number; 2 — bathymetry (in mbsf); 3 — sampling stations; 4 — ^{230}Th/U ages; 5 — contours of proposed unified SMS mound partly covered by sediments where hydrothermal activity have been initiated.*

Table 1. *Description of the SMS samples. Cpy — chalcopyrite; Py — pyrite; Cv — covellite; Ma — marcasite; Sph — sphalerite; Qtz — quartz; Si — amorphous silica; Ba — barite; At — atacamite; Hm — Fe-oxides; ( ) = minor mineral.*

Sample (No.)	Ore body (No.)	Location (N, W)	Water depth (m)	Description	Mineralogy
34L-95M	II	20°07.76’ 45°37.27’	2380	Massive Cu-rich sulfides	Cpy, Qtz, Cv, Py, Hm, (Ba)
34L-95M-1				Massive Fe-rich sulfides	Py, Ma, (Hm)
34L-95M-2				Massive Fe-rich sulfides	Py, Ma, (Qtz), (Cv), (At)
34L-95M-2a				Massive Fe-rich sulfides	Py, Ma, (Hm), (Cpy), (Si)
33L-159M-3	V	19°52.74’ 45°52.99’	2750	Massive Cu-rich sulfides	Cpy, Cv, Py, (Hm), (Si), (At)
33L-41K-2	VI	19°52.41’ 45°52.59’	2970	Sulfide crust	Hm, At, Cv, (Si)
33L-43B-4	VI	19°52.56’ 45°52.68’	2950	Sulfide-bearing breccia	Py, Cpy, At, Hm
33L-43M-3				Massive Cu-rich sulfides	Cpy, Py, Sph, (Ma), (Si)
34L-92M-1	VI	19°52.55’ 45°52.61’	2960	Massive Cu-rich sulfides	Cpy, Hm, (Sph), (At)
34L-176M	VII	19°53.12’ 45°52.35’	2910	Massive Fe-Cu sulfides	Ma, Py, Cv, (Cpy), (Hm), (Ba), (Si)

Analytical methods

The chemical treatment of the samples and the counting techniques for ^{230}Th/U dating are described in Kuznetsov *et al.* (2006). The outer brown oxidation layers of all samples were always removed (recommended by Lalou *et al.*, 1996 and Münch *et al.*, 2001) to avoid problems with contamination. For U and Th analysis, 2 to 4 g of the samples was dissolved in an HCl-HNO$_3$ mixture before a precisely weighed quantity of a spike (^{228}Th-^{232}U at equilibrium) was added. The non-soluble residue was removed by centrifugation. The U and Th fractions were purified and separated by applying anion exchange. Anionite resin AV-17 was used to elute separately the Th and U fractions both dissolved in a 7 n HNO$_3$ using 8 n HCl and a mixture of HNO$_3$ and HCl (0.5 n HNO$_3$, 1 n HCl), respectively. The separated U and Th fractions were finally purified by repeated anion exchange in micro-columns under the same conditions. After that they were electrochemically deposited on separate platinum discs from the ethyl alcohol solution (adding a 0.2 n HNO$_3$ solution) for α counting. The specific ^{238}U, ^{234}U, ^{232}Th, and ^{230}Th activities were measured over several days applying the alpha-spectrometer “Alpha Duo” (ORTEC). The ^{230}Th/U age of the samples was calculated according to the **Eq. 4.1** and given with 1σ standard deviation.

Chemical composition of ores was determined by wavelength-dispersive X-ray spectroscopy using a Spectroscan MAX-GV spectrometer (SPECTRON) equipped with rhodium anode and LiF200, COO$_2$, PET and KAP analyzers. The concentrations of S, Fe, Cu, Zn, Ni, Co, Mn were assessed under the following operation conditions: voltage 40 kV, current 4 mA, count times varied from 15 (Fe) up to 100 sec (Co). The measurement precision was improved to ±7% applying “the thin layer” method which minimizes the matrix effect. The latter reduces the precision of analytical data of materials with extremely varying element composition (Renault and McKee, 1995; Ignatova *et al.*, 2011). The certified reference materials of Cu-rich massive sulfides were used for calibration.

4. ^{230}Th/U DATING METHOD

The SMS deposits have been formed from hydrothermal fluids which originated from circulating seawater in the basalts of the oceanic crust. These fluids contain two orders of magnitude less uranium than seawater (Michard *et al.*, 1983). During mixing of the fluids with seawater the dissolved uranyl-carbonate complexes transform into absorbable uranyl complexes or poorly soluble U^{IV} ions. The latter co-precipitates with transitional sulfides from the fluids. By this, uranium is accumulated in the SMS deposits on the sea floor. Common uranium concentrations in SMS deposits range up to a few tens of ppm (Lalou *et al.*, 1996; Kuznetsov *et al.*, 2006; Kuznetsov and Maksimov, 2012).

There are two prerequisites for ^{230}Th/U dating of SMS deposits: 1) Sulfides contain only uranium without thorium immediately after deposition. 2) During aging, sulfides have behaved under chemically closed conditions with regard to uranium and thorium.

Then, the ^{230}Th/U age of a sample is derived (Kaufman and Broecker, 1965; Ivanovich and Harmon, 1992):

$$\frac{^{230}Th}{^{234}U} = \frac{^{234}U}{^{238}U}\left(1-e^{-\lambda_0 t}\right)+ \frac{\lambda_0}{\lambda_0-\lambda_4}\left(1-\frac{^{234}U}{^{238}U}\right)\left(1-e^{(\lambda_4-\lambda_0)t}\right) \tag{4.1}$$

where: λ_0 and λ_4 are the ^{230}Th and ^{234}U decay constants respectively (Cheng *et al.*, 2000); ^{234}U, ^{238}U, ^{230}Th are specific activities and ^{230}Th/^{234}U and ^{238}U/^{234}U activity ratios (AR); *t* is the age of the sample.

The first prerequisite of ^{230}Th/U dating was fulfilled for samples from active black smokers at 21°N (Lalou and Brichet, 1982) and both the active chimney and the diffuser at 9°50'N along the East Pacific Rise (Kuznetsov *et al.*, 2011). The ^{230}Th and ^{232}Th specific activities of samples with ^{210}Pb/Pb ages < 100 years (half-life is 22.3 yrs) were below the detection limit. Sulfide samples with ages of several tens of thousands of years had no detectable ^{232}Th activity as well (Lalou and Brichet, 1982). Similar results are described from MAR (Lalou *et al.*, 1988, 1996, 1998; You and Bickle, 1998; Kuznetsov *et al.*, 2006, 2011; Kuznetsov and Maksimov, 2012), EPR (Lalou and Brichet, 1982) and the Indian Ridge (Münch *et al.*, 2001; Wang *et al.*, 2012).

In exceptional cases, ^{232}Th is present and monitors the presence of terrigenic matter with non-radiogenic ^{230}Th (Kuznetsov, 1976). In this case deep-sea sediments cannot be dated.

There is evidence that Th is immobile in water and is not kept in solution (Kuznetsov, 1976; Huh and Ku, 1984; Cochran, 1992; Henderson and Anderson, 2003; Kuznetsov and Maksimov, 2012). On the contrary, uranium is easily soluble and post-depositional input or loss of uranium has been often observed albeit. It is however difficult to establish. Related U accumulation or leaching migration results in underestimated and overestimated ^{230}Th/U ages, respectively. Lalou *et al.* (1996) first found that a missing relationship between the uranium concentration and the ^{230}Th/U age of samples from the same site excludes open-system conditions with respect to uranium. Our dates from the Peterburgskoye, Logachev and Semyenov hydrothermal areas (Kuznetsov *et al.*, 2006, 2011) confirm this statement. Two samples from the Logachev-1 field dated separately by Lalou *et al.* (1996) and Kuznetsov *et al.* (2006) agree well despite of very differing U concentrations. By the relationship between U concentration and ^{230}Th/U age, migration of U has to be always excluded.

5. RESULTS

Isotopic and dating results

The results of the radiochemical analyses are given in **Table 2**. The specific ^{232}Th activity was very low in samples 34L-95M, 34L-95M-1, 33L-159M-3 or even below the detection limit in samples 34L-95M-2, 34L-95M-2a, 34L-176M, 33L-43B-4, 33L-43M-3. **Fig. 3** shows that there is no relationship between the specific activity of ^{238}U and the ^{230}Th/U age which excludes open system conditions with respect to uranium.

The ^{234}U/^{238}U AR scatters slightly in the range from 1.029 ± 0.020 (34L-95M-2) to 1.193 ± 0.070 (34L-95M). These values are close to the average value of 1.146 ± 0.002 for seawater (Chen *et al.*, 1986), and indicate the hydrogenous origin of U in these samples. The samples 34L-92M-1 and 33L-41K-2 were not datable because they had a ^{230}Th/^{234}U AR >1.0 and contained ^{232}Th (**Table 1**), indicating contamination with terrigenous material.

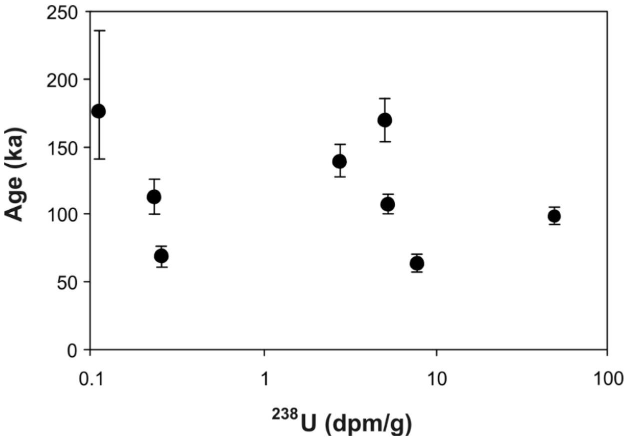

Fig. 3. *The relationship between ^{230}Th/U age vs the ^{238}U specific activity for SMS samples from the Peterburgskoye hydrothermal field confirms closed system conditions with regard to U.*

Table 2. *Results of the radiochemical analyses and ^{230}Th/U ages (both 1 sigma) of the SMS samples from the Peterburgskoye hydrothermal field.*

Sample No.	Ore body (No.)	^{238}U (dpm/g)	^{234}U (dpm/g)	^{230}Th (dpm/g)	^{232}Th (dpm/g)	^{230}Th/^{234}U AR	^{234}U/^{238}U AR	Age (ka)
34L-95M	II	0.231±0.010	0.276±0.011	0.182±0.009	≤0.023	0.661±0.041	1.193±0.070	112.6±14.4/12.3
34L-95M-1	II	5.053±0.129	5.504±0.139	4.416±0.114	≤0.024	0.802±0.029	1.089±0.023	168.9±17.2/14.5
34L-95M-2	II	5.227±0.123	5.379±0.126	3.389±0.089	bdl	0.630±0.022	1.029±0.020	107.2±7.1/6.6
34L-95M-2a	II	2.767±0.093	2.900±0.097	2.110±0.034	bdl	0.728±0.027	1.048±0.035	138.9±12.8/11.1
33L-159M-3*	V	0.111±0.007	0.123±0.007	0.101±0.007	≤0.011	0.820±0.072	1.108±0.091	176.2±59.1/35.7
33L-41K-2	VI	0.875±0.026	0.993±0.028	2.727±0.062	0.107±0.013	2.747±0.099	1.135±0.040	-
33L-43B-4	VI	7.718±0.237	8.231±0.251	3.659±0.157	bdl	0.445±0.023	1.067±0.024	63.3±4.8/4.5
33L-43M-3*	VI	48.244±0.918	51.305±0.975	30.801±0.188	bdl	0.600±0.012	1.064±0.007	98.3±3.3
34L-92M-1	VI	9.173±0.192	9.664±0.201	10.391±0.111	0.154±0.013	1.075±0.025	1.054±0.016	-
34L-176M*	VII	0.254±0.014	0.294±0.015	0.139±0.008	bdl	0.473±0.035	1.157±0.081	68.3±7.8/7.1

** — samples dated earlier (Shilov* et al.*, 2012; Cherkashev* et al.*, 2013).*

Geochemistry

The chemical composition of 9 samples is presented in **Table 3**. Fe, Cu and S are the main constituents of the ores with a total content of 92.0–99.7 wt.%. Only the sample 34L-95 had less (52.3 wt.%) due to secondary sulfide silicification (**Table 1**), indicated by a high SiO_2 content.

The SMS samples contained low concentrations of Zn (from 0.04 to 0.33 wt.%) exept sample 33L-43M-3 with 1.6 wt.%. The concentrations of other elements were low except of sample 34L-92M-1 with parts of percents of Co, Ni and Mn. The sample 33L-43B-4 (sulfide-bearing rock breccia composed of an atacamite-hematite aggregate) had the highest concentration of Cu (32.99 wt.%).

6. DISCUSSION

The previously reported exceptionally old age of 176 ± 59/36 ka of a SMS sample from the Peterburgskoye hydrothermal field (Shilov *et al.*, 2012) was confirmed by the new ^{230}Th/U date of 69^{+17}_{-15} ka (34L- 95M-1). All other dates from the same site provided evidence that the hydrothermal activity lasted from ca. 176 to 63 ka. According to the spatial distribution of the ^{230}Th/U dates the hydrothermal activity and ore-forming processes started in the southeastern part of the field (**Fig. 2**) and might have extended toward the West and North in a long-term multi-stage evolution. More dates are required for a better understanding.

Our ^{230}Th/U dates confirmed the theory by Shilov *et al.* (2012) that at an early stage mounds II-V might have been a single large ore body and later diverted into separate mounds by accumulation of metalliferous sediments in the depressions on this ore body.

The observed variations of the chemical composition of the Peterburgskoye SMS samples is due to different proportions of the main ore-forming minerals: pyrite (marcasite), chalcopyrite and sphalerite. All sample compositions are plotted within the triangle pyrite — sphalerite (covellite) — quartz (hematite) (**Fig. 4**). Most dots scatter along the pyrite-chalcopyrite mixing line. The deviating dot of the sample 33L-43B-4 represents sulfide breccia and might have undergone secondary cementation processes.

Usually SMS samples of individual mounds show a great variety in their chemical and mineralogical compositions (Bogdanov *et al.*, 2006; Hannington *et al.*, 2011), but those from the Peterburgskoye field did not. These sulfide ores had three main components: Fe, Cu and S and traces of Zn with very low concentrations of trace elements (Cherkashev *et al.*, 2013). Such geochemical features are typical for hydrothermal sulfide ores associated with basalts.

Cherkashev *et al.* (2013) have already presumed that the accumulated ore mass increases with age. Our results confirmed the oldest ages of Peterburgskoye field and allowed us to assume that the main ore bodies within this field are most likely buried under sediments and still

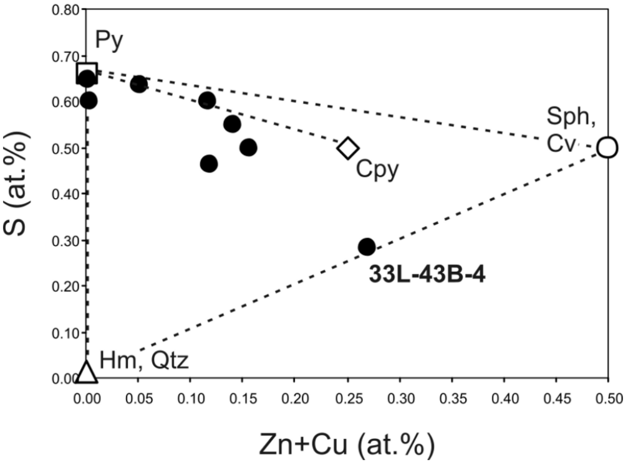

Fig. 4. *S versus Cu+Zn plot (in atomic %) for SMS samples. Dotted line shows relationships between the composition of the main ore forming minerals. Black dots — samples, white symbols — stechiometric compositions of minerals: Py — pyrite (square), Cpy — chalcopyrite (diamond), Sph — sphalerite (circle), Cv — covellite (circle), Hm — hematite (triangle), Qtz — quartz (triangle).*

Table 3. *Chemical composition of sulfides from the Peterburgskoye hydrothermal field.*

Sample No.	Ore body (No.)	S (wt.%)	Fe (wt.%)	Cu (wt.%)	Zn (wt.%)	Ni ppm	Co ppm	Mn ppm
34L-95M	II	18.43	22.30	11.57	0.03	49	505	304
34L-95M-1	II	50.85	48.47	0.20	0.19	47	80	106
34L-95M-2	II	50.42	47.61	0.28	0.11	286	209	250
34L-95M-2a	II	42.62	49.03	0.37	0.05	325	2410	275
33L-159M-3	V	45.03	37.04	17.25	0.14	35	290	106
33L-43B-4	VI	17.41	47.80	32.99	0.04	43	511	139
33L-43M-3	VI	39.67	39.49	18.75	1.60	50	512	548
34L-92M-1	VI	31.66	49.85	15.96	0.33	2248	4758	3993
34L-176M	VII	49.14	42.57	7.94	0.10	41	105	104
Geometric mean		35.84	41.62	4.09	0.13	104	451	269
Multiplicative standard deviation		1.52	1.29	7.90	3.34	4.18	3.81	3.21

remain undiscovered. As for now, available estimates give only 2.9 million tons of SMS (Cherkashev *et al.*, 2013).

7. CONCLUSIONS

Already published and new ^{230}Th/U dates provide evidence that SMS of the Peterburgskoye hydrothermal field is up to 169 ± 17/14 ka old. The field had a long-term multi-stage history between ca. 170 and 63 ka which started in the south-eastern part and diverted presumably to the west and north. Our dates indirectly confirmed the idea that presently separated sulfide mounds were initially in the past a single unified ore body. The oldest hydrothermal ores of this field are represented by pyrite, pyrite-chalcopyrite types and have a chemical composition typical for SMS associated with basalts.

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