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GEOCHEMISTRY

The ^{230}Th/U Dating of Sulfide Ores in the Ocean: Methodical Possibilities, Measurement Results, and Perspectives of Application

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Hydrothermal sulfide ores discovered in 1978 (21° N East Pacific Rise, Pacific Ocean) and 1985 (Mid-Atlantic Ridge) have attracted great scientific and applied interest owing to high concentrations of many useful components (Cu, Zn, Au, and others) in them.

Among various aspects of oceanic hydrothermal processes, the important issue of dating ore-forming stages remains poorly studied. Elucidation of this problem is crucial not only for reconstruction of the initiation and evolution of ore formation, but also for solution of several essential issues. Isotope geochronology of sulfide ores and metalliferous sediments is the main tool used for the dating.

The initial results of the geochronological investigation of sulfide ores from the MAR by ^{210}Pb/Pb (dating limit 0–200 yr) and ^{230}Th/U (dating limit ~2000–250 000 yr) methods were reported by Lalou et al. [1, 2]. The age boundaries and duration of stages of hydrothermal activity were also recorded using ^{14}C dating of interlayers of metalliferous sediments [3–5].

Nevertheless, published data on the frequency and duration of periods of hydrothermal activity are still scanty, particularly due to insufficient substantiation of the validity of methods of isotope geochronological dating.

Therefore, we put forward the following tasks: (1) development of the main theoretical principles of the ^{230}Th/U method for its implementation in the dating of oceanic sulfide ores; (2) gathering of the first Russian data on the age of ore samples and formulation of preliminary conclusions concerning the temporal evolution of hydrothermal processes in the MAR.

We analyzed sulfide samples taken from several hydrothermal fields of the MAR. Samples from hydrothermal fields 16°38′ N (16°38.5′ N, 46°28.5′ W), Logatchev-1 (14°45.2′ N, 44°58.8′ W), Logatchev-2 (14°43.2′ N, 44°56.2′ W), Ashadze-1 (12°58.5′ N, 46°28.5′ W), and Ashadze-2 (12°59.3′ N, 44°54.45′ W) were taken during cruises of R/V *Professor Logatchev*. Samples from the Rainbow hydrothermal field (38°13.1′ N, 33°54.3′ W) were taken during the cruise of R/V *Akademik Keldysh*.

In order to solve the first issue, we carried out radiochemical analyses of massive sulfide ore samples and investigated the behavior of U and Th isotopes in them. We also developed theoretical principles of the application of the ^{230}Th/U method for the dating of ore formations.

U and Th isotopes were extracted from the analyzed samples by the following procedure: transfer of weighed portions (n g) to the HNO_3–HCl solution; removal of the minor residue; precipitation of radionuclides together with iron hydroxide; separation (and purification) of the uranium and thorium fractions by anionic chromatography; and electric precipitation of each fraction from the alcohol solution on the Pt target [6]. Alpha-spectrometric measurements were carried out for several days. The table presents the results of the radiochemical analysis, including the dating of each sample.

According to [7, 8], dating of sulfide ore samples by the ^{230}Th/U method is based on the following two theoretical principles: (1) sulfides precipitating from hydro-

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Results of the radiochemical analysis and ^{230}Th/U dating of sulfide ore samples

Sample no.	^{238}U, 10^{-6} g U/g sample	^{238}U, 10^{-6} g U/g sample, decay/min · g	^{234}U, decay/min · g	^{234}U/^{238}U	^{232}Th, decay/min · g	^{230}Th, decay/min · g	^{230}Th/^{234}U	Age, ka
Logatchev-1 hydrothermal field								
6/3	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
9/2	0.91 ± 0.04	0.66 ± 0.03	0.75 ± 0.03	1.13 ± 0.03	<0.001 tr.	0.11 ± 0.01	0.143 ± 0.008	16.8 ± 1.0
6/3 [8]	13.01 ± 0.65			1.09 ± 0.02	0.072 ± 0.070		0.42 ± 0.025	58.6 ± 4.6
9/2 [8]	0.68 ± 0.04			1.16 ± 0.07	<0.004		0.142 ± 0.017	16.5 ± 2.1
Logatchev-2 hydrothermal field								
384-4	3.37 ± 0.27	2.43 ± 0.20	2.43 ± 0.20	1.05 ± 0.05	<0.001 tr.	0.09 ± 0.01	0.035 ± 0.004	3.9 ± 0.4
Rainbow hydrothermal field								
42 AMK 3982-M1-3a	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
42 AMK 3982-M1-4b	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
42 AMK 3982-M1-2/5	0.06 ± 0.01	0.044 ± 0.004	0.050 ± 0.004	1.13 ± 0.14	n.d.	<0.009	<0.181	<22.0
42 AMK 3982-M1-6	0.24 ± 0.01	0.17 ± 0.01	0.21 ± 0.01	1.21 ± 0.08	n.d.	0.007 ± 0.001	0.035 ± 0.005	3.9 ± 0.6
16°38′ N hydrothermal field								
1243-M-1	1.19 ± 0.04	0.86 ± 0.03	1.09 ± 0.03	1.27 ± 0.05	0.006 ± 0.001 tr.	0.29 ± 0.01	0.267 ± 0.011	33.3 ± 1.7
1260-M-4	2.24 ± 0.07	1.61 ± 0.05	1.88 ± 0.05	1.17 ± 0.03	n.d.	0.83 ± 0.01	0.440 ± 0.013	61.9 ± 2.8
1266-M	2.18 ± 0.07	1.57 ± 0.05	1.75 ± 0.05	1.12 ± 0.03	0.033 ± 0.004	0.77 ± 0.02	0.438 ± 0.018	61.8 ± 3.7
1269-M-1	6.80 ± 0.21	4.90 ± 0.15	5.29 ± 0.16	1.08 ± 0.03	0.022 ± 0.004	2.40 ± 0.05	0.454 ± 0.017	65.1 ± 3.7
1269-T-6/2	1.39 ± 0.06	1.00 ± 0.04	1.26 ± 0.05	1.25 ± 0.06	<0.003 tr.	0.35 ± 0.01	0.280 ± 0.012	35.3 ± 1.8
1271-T-1	3.64 ± 0.14	2.62 ± 0.10	3.00 ± 0.11	1.14 ± 0.05	<0.007 tr.	0.95 ± 0.03	0.316 ± 0.015	40.9 ± 2.5
1271-T-9	0.79 ± 0.03	0.57 ± 0.02	0.75 ± 0.03	1.31 ± 0.06	<0.006 tr.	0.22 ± 0.01	0.298 ± 0.012	37.8 ± 1.9
Ashadze-1 hydrothermal field								
1319-T-1	0.63 ± 0.03	0.45 ± 0.02	0.52 ± 0.02	1.16 ± 0.07	n.d.	0.029 ± 0.007	0.056 ± 0.013	6.2 ± 1.5
1319-T-2	0.26 ± 0.02	0.19 ± 0.02	0.24 ± 0.02	1.27 ± 0.12	n.d.	0.015 ± 0.004	0.064 ± 0.016	7.2 ± 1.8
1312-T-2	0.46 ± 0.03	0.33 ± 0.02	0.40 ± 0.02	1.19 ± 0.09	n.d.	0.018 ± 0.003	0.045 ± 0.008	5.0 ± 0.9
1021-T	1.16 ± 0.06	0.84 ± 0.04	0.99 ± 0.05	1.19 ± 0.07	n.d.	0.019 ± 0.003	0.019 ± 0.003	2.1 ± 0.3
Ashadze-2 hydrothermal field								
1498-MP-4	2.06 ± 0.07	1.48 ± 0.05	1.78 ± 0.06	1.20 ± 0.04	The same	0.331 ± 0.014	0.186 ± 0.010	22.2 ± 1.3
1498-M-33	5.34 ± 0.16	3.84 ± 0.11	4.22 ± 0.12	1.10 ± 0.03	The same	0.748 ± 0.023	0.177 ± 0.008	21.1 ± 1.1
1447-1-T	12.63 ± 0.24	9.10 ± 0.17	10.44 ± 0.19	1.15 ± 0.01	The same	1.128 ± 0.026	0.108 ± 0.003	12.4 ± 0.4
1498-2-M	10.44 ± 0.24	7.52 ± 0.17	8.15 ± 0.19	1.08 ± 0.02	The same	1.174 ± 0.021	0.144 ± 0.004	16.8 ± 0.6
1535-1-P	0.86 ± 0.07	0.62 ± 0.05	0.71 ± 0.05	1.14 ± 0.11	The same	0.138 ± 0.010	0.195 ± 0.020	23.4 ± 2.8

Note: (tr.) Traces; (n.d.) not detected.

thermal solutions should contain U without its daughter radionuclide ^{230}Th; (2) sulfides should represent closed geochemical systems relative to U and Th.

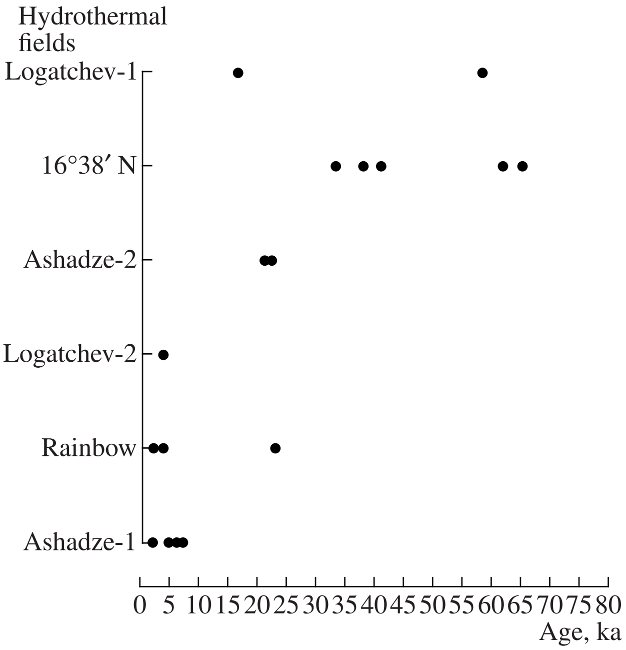
The results obtained show that ^{232}Th occurs in the samples as a negligible or trace component. In some cases, its content (specific activity) is below the detection limit. According to [9], ^{232}Th is present in the oceanic medium mainly in the suspended mineral substance delivered from continents, suggesting that this radionuclide can be considered an indicator of a terrigenous source. Therefore, data on ^{232}Th in samples indicate that terrigenous ^{232}Th, ^{230}Th, ^{238}U, and ^{234}U isotopes are virtually absent in leachates of the samples. Hence, virtually the whole amount of ^{230}Th detected in sulfide deposits is a radiogenic material formed in hydrothermal ores from the parental radionuclides ^{234}U and ^{238}U. In [2, 8, 10], Lalou et al. demonstrated convincingly that the first requirement for U–Th dating of sulfide deposits can be fulfilled. For example, the age of sulfide samples from the EPR based on unsupported lead (^{210}Pb/Pb) is estimated at <100 yr, whereas the contents of both Th isotopes are below the detection limit. In contrast, ~35-ka-old samples lack ^{210}Pb (half-life ~22 yr) and contain appreciable ^{230}Th. Activity of ^{232}Th is not recorded. Thus, our results and the literature data suggest that the first requirement for the application of the U–Th method can be fulfilled.

According to [8], reducing conditions in some zones of hydrothermal activity foster the precipitation of seawater-hosted U together with metal sulfides transported by hydrothermal fluids to the surface. The active hydrothermal field always maintains local reducing settings in the course of evolution and promotes the transition of U into the solid phase and its preservation in the sulfide body (substrate). However, the lack of any systematic correlation between the U content and the age of coeval (within the error limit) samples from a single hydrothermal field testifies to the absence of input or output of U in the sulfide–seawater system [8]. For example, datings of sulfides from the same stations of the Logatchev-1 hydrothermal field obtained in our and previous works [8, 11] appear virtually identical, although the contents of U and Th in both cases are different (table). Lack of migration of Th isotopes in various types of oceanic sediments and the sorption susceptibility of this element in the form of hydroxycomplexes is demonstrated in [9, 12]. Therefore, we believe that this radioelement (primarily, ^{230}Th) located in the solid phase of sulfide deposits can hardly be transported with interstitial waters. Thus, the second requirement for the U–Th method (the presence of a closed geochemical system in the sample relative to U and Th) is also sufficiently substantiated.

Therefore, we can conclude that application of the ^{232}Th/U method is valid for the dating of sulfide deposits.

Our results of the dating of sulfide ore samples (table, figure) can be used for various purposes. First, we determined the total age range for the sulfide ore samples (~65 ka). The oldest ores of this age occur in the 16°38′ N hydrothermal field. Second, we can tentatively recognize four stages of the hydrothermal activity (figure): a recent stage (0–7 ka) and three older stages (16–23, 33–40, and 58–65 ka, respectively).

Evidently, we cannot outline the stages mentioned above confidently because of an insignificant number of datings. An increase in statistical data will make it possible to elucidate the presence of a correlation between periods of hydrothermal activity and the associated ore formation in the MAR scale. However, one can distinctly see that the duration of periods of hydrothermal activity was shorter than that of attenuation periods, suggesting a pulse-type mode of hydrothermal activity.



The ^{230}Th/U dating of sulfide ore samples from hydrothermal fields in the MAR.

Correlation of the age of ore fields with their dimension is another interesting and important aspect of our results. Previous comparative data on the size and age of ore fields in the MAR [13] suggest that the time parameter is crucial for the scale of ore formation. Given that the ore material is regularly delivered, the volume of ore material accumulated in hydrothermal edifices shows a direct correlation with the duration of functioning of an ore-generating system. This fact reflects the applied significance of datings of sulfide deposits. If the samples are old enough, we can hope that the orebody (and its resources) will be sufficiently large.

The results of U–Th dating of sulfide samples and the available literature data open new scopes for the application of ^{230}Th/U dating of such deposits for studying the evolution of oceanic ore formation in the course of the last 250–300 ka (dating limit of the method). For this purpose, one should carry out a more comprehensive investigation of hydrothermal fields. For example, combination of data on ^{230}Th and ^{14}C datings, chemical analysis, lithology, and biostratigraphy of sedimentary columns from zones of hydrothermal activity will make it possible to outline metalliferous interlayers and temporal boundaries of the hydrothermal activity. Application of the ^{230}Th geochronological method expands the range of age determination for metalliferous sediments to 250–300 ka [6]. Dating of samples from sulfide edifices in these hydrothermal zones will make it possible to refine the age characteristics of sedimentary cores. In other words, comparison of datings of metalliferous sediments and sulfide ores can make it possible to determine their temporal variations in composition and significantly refine the evolution of hydrothermal ore formation in the course of the last 250–300 ka.

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