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GEOLOGY

Tellurium and Thallium in Ferromanganese Crusts and Phosphates on Oceanic Seamounts

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Tellurium and thallium are among the least widespread elements in the Earth. According to [1–4], their contents in the Earth's crust, in general, and igneous and sedimentary (including oceanic) rocks, in particular, vary from <1 to *n* mg/t. These metals attract special attention from geologists and geochemists because of their very high (four orders of magnitude or more) concentrations in some rocks. In oceans, such rocks are represented by ferromanganese crusts (hereafter, crusts) that make up extended sheets on the surface of many seamounts with summits located at a depth of more than 1–2 km.

Therefore, the crusts can serve as a promising raw material for Co and base metals. The crusts also contain other metals that can be extracted as valuable byproducts or hazardous (in terms of technology or ecology) trace elements. Tellurium and thallium have both these properties: they are widely applied in modern nanotechnology, on the one hand, and characterized by high toxicity, on the other hand.

The presence of Te in oceanic sediments was first reported by Leikin in 1963 [3]. He detected Te (5–125 ppm) in some ferromanganese nodules that are compositionally similar to crusts. Analogous or higher Te contents (up to 270 ppm) were reported in [6, 7]. Analysis of 105 samples of crusts from various regions of the Pacific, Atlantic, and Indian oceans confirmed the previous data. The Te content in genetically different crusts varies from 0.06 to 205 ppm [4].

In contrast to Te, Tl has been investigated more comprehensively since 1958 [8]. According to reviews presented in [2, 3], the Tl content in ferromanganese nodules and crusts varies from 1 to 675 ppm. The Tl content in oceanic sediments (0.003–6 ppm) is comparable to the Te content.

Despite the available data, the association of Te and Tl with ore-forming components in the ferromanganese nodules and crusts remains a debatable issue. The relationship between these elements has not been examined at all.

In order to fill this gap, we carried out a comprehensive analysis of ferromanganese nodules and crusts, as well as gangue minerals in them, in samples taken from seamounts in the Pacific and Atlantic oceans. The present paper reports data on the contents of Fe, Mn, Co, Ce, Tl, and Te in the analyzed material.

The Pacific material is represented by crusts from seamounts located in the central northern tropical zone of the Mid-Pacific, as well as compositionally similar crusts and nodules from the Magellan Mountains in the western area of the same zone. The Atlantic material was recovered from the Sierra Leone Seamount (eastern tropical zone of the ocean) and some sites in the Mid-Atlantic Ridge (MAR). The geological setting and ore deposits of these regions are described in [3, 9, 10]. We studied not only the ore material, but also the phosphate fraction (interlayers and inclusions in crusts). The slightly mineralized cores of nodules were also examined. For the sake of comparison, we also analyzed two nodules from the eastern Baltic Sea. In total, 48 samples were analyzed.

The author collected materials from the Mid-Pacific seamounts and the Baltic Sea during Cruise 48 of the R/V *Vityaz* and Cruise 9 of the R/V *Akademik Sergei Vavilov*. Other samples were taken by M.E. Mel'nikov (Magellan Mountains), V.Kh. Gevorkyan (Sierra Leone Rise), and L.V. Dmitriev (Mid-Atlantic Ridge).

The contents of trace elements in the crusts were determined in the Chemical Laboratory of the Shirshov Institute of Oceanology, Moscow (N.N. Zavadskaya, analyst). The contents of Ce, Te, and Tl were determined at the Analytical Certification Center of the Fedorovskii All-Russia Research Institute of Mineral Resources (Moscow) under the supervision of V.K. Karandashin.

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Table 1. Chemical composition of crusts and nodules and inclusions therein

Region, material	Fe, %	Mn, %	Co, %	Ce, ppm	Te, ppm	Tl, ppm	*N*
Mid-Pacific, crusts	8.8–14.3 (11.07)	10.7–24.0 (16.0)	0.22–1.37 (0.62)	759–1326 (922)	37–97 (53)	44–230 (121)	7
Phosphate inclusions	0.21–5.3 (1.54)	0.04–1.25 (0.44)	0.002–0.033 (0.009)	6–100 (35)	0.53–3.1 (1.7)	0.21–6.1 (2.54)	8
Magellan Mts., crusts	11.2–16.4 (14.5)	17.6–24.8 (20.6)	0.22–0.57 (0.455)	690–1600 (985)	46–83 (62)	86–190 (140)	6
Phosphate inclusions	0.16–3.8 (1.6)	0.08–0.90 (0.48)	0.001–0.013 (0.007)	7–96 (47)	0.2–3.5 (1.8)	<1–4.1 (2.1)	3
Nodules	12.6–15.2 (14.4)	20.5–24.2 (22.9)	0.56–0.65 (0.61)	690–810 (760)	31–48 (38)	150–220 (182)	5
Nodule core	11.0 12.5	1.0 1.1	0.023 0.023	60 43	2.6 8.0	9.2 7.6	1 1
Sierra Leone, crusts	10.4–17.6 (13.7)	17.1–21.6 (19.4)	0.554–0.765 (0.680)	1537–1927 (1686)	61–88 (74)	119–188 (145)	3
Phosphate inclusions	0.38–1.7 (0.97)	0.14–1.8 (0.73)	0.005–0.014 (0.022)	15–159 (64)	1.0–4.8 (2.7)	1.3–19.4 (8.0)	3
MAR, crusts	13.3–23.1 (18.1)	11.7–17.5 (15.1)	0.32–1.10 (0.62)	1400–2700 (2030)	27–91 (49)	100–180 (132)	7
Baltic Sea, nodules	34.2 5.9	2.13 34.0	0.006 0.008	95 94	0.44 0.58	4.6 4.0	1 1
Average							
Crusts in the Pacific Ocean	12.65	18.1	0.54	951	57.4	129	13
Crusts in the Atlantic Ocean	16.8	16.4	0.64	1920	56.3	135	10
All crusts	14.4	17.3	0.58	1372	56.9	132	23
Crusts and nodules in the Pacific Ocean	13.1	20.2	0.56	898	57.3	199	18
All phosphates	1.56	0.45	0.0086	39	1.75	2.4	14

Note: Average value is given in parentheses; (*N*) number of samples.

The contents of elements in the oceanic crusts and nodules show the following variation range (Table 1): Fe 8–18.1%, Mn 10.7–24.2%, Co 0.22–1.37%, Ce 690–2700 ppm, Te 27–97 ppm, and Tl 44–230 ppm. The variation range is maximal in crusts from the Mid-Pacific seamounts.

The phosphate fraction of the crusts is depleted in all these elements: Fe 0.16–5.3%, Mn 0.04–1.8%, Co 0.002–0.033%, Ce 6–159 ppm, Te 0.2–4.8 ppm, and Tl 0.21–19.4 ppm.

Two nodule cores from the Magellan Mountains show similar or identical contents of Fe (11.0–12.5%), Mn (1.0–1.1%), Co (0.023%), Ce (43–60 ppm), and Tl (7.6–9.2 ppm). However, the Te content varies from 2.6 to 8.0 ppm.

Two ferromanganese nodules from the Baltic Sea are characterized by different compositions: Fe 34.2 and 5.9%, Mn 2.13 and 34.0%. However, the contents of other elements are virtually similar: Co 0.006–0.008%, Ce 95–96 ppm, Te 0.44–0.58 ppm, and Tl 4.0–4.6 ppm.

Comparison of the average contents of elements in the oceanic crusts and nodules from various regions revealed the following regularity: the Fe content is minimal (11.07%) in the Mid-Pacific crust and maximal (18.1%) in the MAR crust, while the Mn content is minimal (15.1%) in the MAR crust and maximal (22.9%) in the Mid-Pacific crust. The Co content is minimal (0.45%) in the Magellan crust and maximal (0.68%) in the Sierra Leone crust. The Ce content is minimal (760 ppm) in the Magellan nodules and maximal (2030 ppm) in the Sierra Leone crust. The Te content is low (38 ppm) in the Magellan crust and high (74 ppm) in the Sierra Leone crust. The Ta content is low (121 ppm) in the Mid-Pacific crust and high (182 ppm) in the Magellan nodule.

In general, relative to the Atlantic crusts, the Pacific counterparts are depleted in Fe, Co, and Ce. They are slightly enriched in Mn, as was indicated in [3, 7, 11].

Table 2. Ratios of average concentrations of elements in the studied material, sediments, basic rocks, and oceanic water

Material	Mn/Fe	Fe/Tl	Fe/Te	Mn/Tl	Mn/Te	Tl/Te	Co/Tl	Co/Te	Ce/Tl	Ce/Te	Co/Ce
1	1.45	900	2000	1300	3000	2.28	51	117	7.6	17.4	6.7
2	1.42	1000	2300	1500	3300	2.26	32	73	7.0	16.0	4.6
3	1.42	940	1850	1340	2620	2.0	47	92	12.6	23.0	4.0
4	0.81	1370	3700	1140	3080	2.7	47	155	15.4	41	3.0
5	1.59	790	3800	1260	6000	4.8	33	160	4.2	20	8.0
6	0.28	6100	9060	1760	2600	1.5	35	53	14	20	2.6
7	0.30	7600	8900	2300	2700	1.2	33	39	22	26	1.5
8	0.75	1250	3600	910	2700	3.0	27	81	8	24	3.4
9	0.09	$12 \cdot 10^3$	$42 \cdot 10^3$	1090	3800	3.5	25	88	6.5	23	3.8
10	0.09	$16.5 \cdot 10^3$	$15.6 \cdot 10^3$	1450	1380	0.95	30	21	5.6	5.3	5.3
11	0.06	$74 \cdot 10^3$	$8 \cdot 10^5$	4630	$48 \cdot 10^3$	10.4	13	136	20	216	0.63
12	0.58	$14.7 \cdot 10^3$	$1 \cdot 10^5$	$85 \cdot 10^3$	$6 \cdot 10^6$	6.9	20	138	23	162	0.85
13	1.31	1000	2500	1300	3000	2.6	42	109	9.0	23	4.7
14	2.8	7000	9000	1900	2500	1.8	32	57	16	19	2.0
15	0.08	$2 \cdot 10^4$	$4 \cdot 10^4$	1700	3000	1.8	36	65	55	100	0.6
16	0.02	$4 \cdot 10^5$	$8 \cdot 10^7$	$1 \cdot 10^4$	$2 \cdot 10^6$	200	225	4500	22	450	10
17	0.5	4.7	9.3	2.3	45	20	0.1	2	0.23	4.7	0.4

Note: (1–4) Crusts from seamounts: (1) Mid-Pacific, (2) Magellan Mts., (3) Sierra Leone, (4) MAR; (5) nodules from the Magellan Mts.; (6–8) phosphates from crusts: (6) Mid-Pacific, (7) Magellan Mts., (8) Sierra Leone; (9, 10) cores of nodules from the Magellan Mts.; (11, 12) nodules from the Baltic Sea; (13) all crusts; (14) all phosphates; (15) oceanic sediments; (16) basic rocks; (17) oceanic water.

However, they have virtually similar contents of Te (56.3–57.4 ppm) and Tl (129–135 ppm). Crusts from other regions of the Pacific and Atlantic oceans also have similar Te contents [4].

All oceanic ferromanganese nodules and crusts are characterized by the following average contents of elements: Fe 14.4%, Mn 18.1%, Co 0.59%, Ce 1266 ppm, Te 54 ppm, and Tl 141 ppm.

In order to compare the composition of crusts with the composition of oceanic water, sediments, and igneous rocks, it is expedient to examine the contents of elements and ratios of typical elements. For example, discrepancies in the contents of elements can reach several orders of magnitude, while the ratios of elements change gradually. Therefore, the ratios of elements reflect the general trend and they can be used as an autonomous informative parameter.

Table 2 presents average Mn/Fe, Fe/Tl, Fe/Te, Mn/Tl, Mn/Te, Tl/Te, Co/Tl, Co/Te, Ce/Tl, Ce/Te, and Co/Ce ratios in all types of ore and barren formations, as well as oceanic deep-water sediments [2], basic rocks [1], and oceanic water [12].

These ratios are closest in the crusts and nodules. This fact testifies to the genetic similarity of these formations and refutes the earlier concept of principally different sources for ore material and formation mechanisms.

In addition, the ratios of elements in the crusts and associated phosphates with the impregnation of ferromanganese hydroxides are also very similar. Hence, the concentration of several metals (e.g., Te and Tl) in phosphates from the seamounts is primarily related to the presence of ore components in the phosphate material and unrelated to their sorption by the apatite phase.

It is interesting that the Tl/Te, Mn/Tl, Mn/Te, Co/Tl, and Co/Te ratios are similar in the deep-sea sediments, crusts, nodules, and phosphates. This fact indicates a certain uniformity in the behavior of Mn, Co, Te, and Tl in the global process of pelagic oceanic sedimentation. In terms of physical and geochemical parameters, the behavior of metals mentioned above differs radically from the process of sedimentation at continental submarine margins, where terrigenous sedimentation prevails over the delivery of dissolved forms of elements from the seawater [13, 14].

In our case, we could not carry out quantitative assessment of the hydrothermal factor in the marine geochemistry of Te. The Te content appeared to be <0.3 ppm in five samples of hydrothermal manganese crust taken from the Yamato Rise (Sea of Japan). Therefore, this result was not included in Table 1. The Te content varies from 0.06 to 1 ppm in 10 samples of crusts taken from other zones of hydrothermal activity (the Mariana, Yap, and Tonga volcanic arcs; the Lau and Fizi back-arc spreading centers; the Hawaiian and Galapagos spreading zones; and the Blanco transform fault) [4]. This fact also testifies to low mobility of Te in the oceanic hydrothermal process.

The Ta content varies from 0.4 to 21 ppm (average 7.6 ppm) in five samples of the hydrothermal crust taken from the Sea of Japan. This value is appreciably lower than the content in hydrothermal crusts from other oceanic zones (average 29 ppm, based on 13 samples [7]). In our samples, contents of Mn and Fe are 22.5–33.3 and 0.26–7.70%, respectively. Tl and Fe demonstrate a distinct correlation, while Tl and Mn lack any correlation. The selective dissolution of two hydrothermal crust samples from the Fizi Basin showed that virtually the whole Tl is transferred to the solution together with Mn, while Te is connected with both manganese and iron phases [15]. Such contradictory results indicate that a more comprehensive investigation is essential for elucidation of the hydrothermal transport of Te and Ta to the ocean.

The mechanism of Te and Tl accumulation in the crusts and nodules is also an open issue. The stability of ratios of Te and Tl with Mn in the crusts testifies to the presence of a significant correlation between both elements. Therefore, we can assume that the manganese phase plays an important role as the carrier of these elements. This correlation is also indicated by the following fact. In contrast to the Te/Mn and Tl/Mn ratios, the Te/Fe and Tl/Fe ratios show a wide range (Table 2). However, investigation of analogous materials from other regions revealed four types of correlation of Te with major elements. The correlation is weak with Mn in the Atlantic crust, weak or significant with both Mn and Fe in crusts from the central Pacific, and strong with Fe in crusts from the western continental margin of the United States (correlation with Mn is absent) [4].

According to recent data [4, 15], the manganese phase of crusts and nodules has a strong negative charge, while the iron phase has a positive charge. Therefore, Mn cations and Fe anions are extracted from ocean water. However, the process is complicated by redox reactions in the case of elements with variable valence (Tl, Te, Co, Ce, and others). Manganese hydroxides are more active oxidizers than iron hydroxides.

In oceanic water, Tl occurs mainly as Tl^+ ions. $TlCl_4^-$, $TlCl^0$, and $Tl(OH)_3^0$ ions are subordinate phases. According to different authors, Te can occur in more diverse forms, such as TeO_3^{2-}, $HTeO_3^-$, $H_5TeO_6^-$, $Te(OH)_6^0$, $TeO(OH)_3^-$, and $TeO(OH)_5^-$ [4, 12, 15]. Therefore, manganese and iron phases of crusts can accumulate mainly Tl and Te, respectively. In order to check this assumption, we used experimental data on the fractionation of crusts into sorbed elements, as well as the manganese, iron, and residual fractions. The results showed the following regularity: approximately 30% Tl is transferred to the manganese fraction (Te is absent); >50% Tl (~5% Te) is transferred to the iron fraction; and <10%Tl (~90% Te) is transferred to the residual fraction [4, 15]. Thus, experimental data on the selective dissolution of ferromanganese crusts confirm the sorptional mechanism of Te and Tl accumulation from seawater by the iron (Fe) and manganese (Mn) phases.

According to [4], the crust extracts complex ions (primarily, as Te^{4+}) from oceanic water. The ions are oxidized by iron hydroxide into Te^{6+}, resulting in a significant intensification of Te accumulation.

Our results indicate the correlation of Te with Mn in some samples. Te also correlates with Co, which, in turn, correlates with Mn. These peculiar correlations remain an open issue. As was indicated by the researchers mentioned above, the problem of the geochemistry of Te and Tl in oceanic ferromanganese ore formation can only be solved based on modern high-precision experimental works devoted to the sorption of these metals from seawater.

The major complications in this issue are as follows: both Te and Tl can exist in seawater as cationic, anionic, and neutral complexes. Their role in reactions depends on the local hydrochemical setting. In addition, physical properties, crystallinity of the rock-forming minerals, and other parameters of crusts are extremely variable in different layers. This fact is not always taken into consideration in experiments.

Based on the present state of knowledge in this field, including the results described above, we can make the following conclusion. In hydrogenetic ferromanganese crusts, Tl is mainly associated with the manganese phase, whereas Te can be associated with both manganese and iron phases. Both metals are members of the group with the maximal concentration in the ferromanganese crust (relative to the Earth's crust), oceanic sediments, and water. The relative stability of the average Te/Tl ratio and ratios of these metals with Mn and Co in the ferromanganese crusts, associated phosphates, and deep-water sediments suggests that all these metals were delivered to sediments by a rather similar mechanism that fostered the precipitation of metals from oceanic water.

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