

Sources of Ore-Forming Fluid in Fumaroles of Kudryavyi Volcano, Kuril Islands: Pb Isotopic Composition of Gas Condensates and Sublimate Minerals

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Kudryavyi Volcano is an example of the modern ore-forming system related to island-arc andesite volcanism. A direct study of high-temperature gas–hydrothermal process in the volcanic edifice is of fundamental significance for understanding the formation conditions of ore deposits in the modern recycling zones of the oceanic crust. This research was aimed at determining the sources of ore matter during formation of polymetal mineralization on the fumarole fields of Kudryavyi Volcano.

Subduction at convergent plate margins is a complex geodynamic setting involving deep-seated interaction and transformation of sediments, the asthenospheric mantle, and oceanic and continental crusts. The differences in isotope characteristics of these geochemical reservoirs make it possible to decipher the genesis of magmatic and ore-forming systems spatially related to the areas of modern island-arc volcanism on the basis of the isotopic composition of Sr, Nd, Pb, Os, and some other elements.

Previous H, He, and C isotope studies of fumarole gases showed that the main fluid sources of the Kudryavyi volcanic system could be subducted sediments of the Pacific floor and mantle wedge [1, 2]. The Nd, Sr, and Pb isotopic composition of the magmatic rocks of Kudryavyi Volcano [3] points to the leading role of a source having Pacific MORB-type isotope–geochemical characteristics. By contrast, a significant contribution of sedimentary rocks was proposed to explain the high Re contents in the high-temperature fluid and ^{187}Os enrichment of basaltic andesites of Kudryavyi Volcano [4]. Wide compositional variations and crystallization temperatures of melt inclusions in

the volcanic rocks of the Medvezh'ya Caldera reflect different sources and heterogeneity of the melts in magma chambers [5].

The Kudryavyi basaltic andesite volcano was formed within the large Medvezh'ya Caldera in the northern part of Iturup Island. The younger basaltic lava flows related to an eruption in 1883 are confined to the western crater of the volcano, whereas stationary high-temperature degassing has been observed over more than 100 yr within the adjacent eastern crater. The mineralization of high-temperature fumarole fields of the volcano demonstrates high accumulation of trace (W, Mo, Re, In, Cd, and Bi), base (Pb, Cu, and Zn), and noble (Au) metals. The chemical composition of the highest temperature gas (940°C) is typical of fluid derivatives of the andesite magmas. Its main components are H_2O and compounds of C and S (approximately 2 mol % each), 0.8 mol % HCl, and up to 1.6 mol % H_2 . The main anions of gas condensate are SO_4^{2-} (up to 13 g/l), F^- , Cl^- (up to 12 g/l), Br, and NO_3^- , as well as thio- and polysulfates [1, 6].

This paper presents results of the Pb isotope study of high-temperature gas condensates and some lead minerals (galena and cannizzarite) from sublimates of the fumarole fields of Kudryavyi Volcano. In addition, a sample of fresh volcanic glass from the basaltic andesite of the youngest Chernysh flow (1883 yr) was analyzed. We took condensate samples during fieldwork in 2001–2004 from three fumarole channels (points 21, 02, and 61) with temperatures ranging from 420 to 720°C. Mineral phases—galena (PbS) and cannizzarite ($\text{Pb}_4\text{Bi}_6\text{S}_{13}$)—were hand-picked from points 24, 62, and 67 (Fig. 1). The Pb content in the gas condensate samples was determined by the ICP-MS method on a Plazma Quad-2 analyzer. The Pb–Pb investigation included the stage of chemical preparation of samples, separation of Pb by the method of ion-exchange chromatography, and analysis of the isotopic composition was measured on a Sector 54 (Micromass, Great Britain)

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thermal ionization mass spectrometer. A 50-ng Pb sample was loaded on a Re filament using the silica gel loading technique. Mass discrimination was determined by systematic measurements of the NIST SRM-981 standard, and correction was made using the linear law of mass fractionation. The coefficient of mass discrimination per mass unit was 0.0004 ± 2 . The total error in Pb isotope ratios obtained was no more than 0.05% per atomic mass unit.

The Pb content in condensates taken from different fumarole channels ranged from 10n to 1500 $\mu\text{g}/\text{kg}$. The highest Pb contents were established in the highest temperature fumaroles. Monthly monitoring of the same fumarole channel with a constant temperature regime showed that the Pb content in the condensate can differ by almost two times. Separate analysis of condensate and its filtrate showed that about one-fourth of the total Pb is precipitated on the filter; i.e., it occurs in condensates in insoluble form.

Due to the high fugacity of lead compounds (including its chloride, considered the predominant species for Pb transport in felsic gas fluid), its mineral phases are precipitated from gas at temperatures below 600–650°C. Galena was first to precipitate. With further temperature decrease within an interval of 620–250°C, galena is supplemented with various Pb–Bi sulfosalts. The lowest temperature phases are chlorides and sulfates of Pb and K–Pb.

The table shows Pb–Pb isotope characteristics of gas condensate and sublimate minerals from the fumarole fields of Kudryavyi Volcano and volcanic glass. The studied samples demonstrate a homogeneous Pb isotopic composition. The scale of observed differences in isotope ratios, which can be estimated from the mean standard deviation (σ , %) is 0.08% for $^{208}\text{Pb}/^{204}\text{Pb}$ and no more than 0.02 and 0.04% for $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, respectively. The obtained estimates of scatter for all ratios are lower than the analytical errors. Thus, the differences recorded in Pb isotopic composition are defined by analytical factors and do not reflect its geochemical heterogeneity. This attests to the high homogeneity of Pb isotopic composition in gas condensates and sublimates of the fumaroles of Kudryavyi Volcano.

The Pb–Pb isotopic composition of the products of fumarole activity of Kudryavyi Volcano indicates evolution of Pb in the geochemical reservoir with relatively low U/Pb and Th/Pb ratios prior to its delivery to the ore-forming system. The calculated value of the evolution parameter $\mu_2 = ^{238}\text{U}/^{204}\text{Pb}$ for the initial Pb source of the fumarole gases was 9.1–9.4.

The Pb–Pb diagrams show the comparison between the Pb isotopic compositions of the fumarole gases and those of the rocks that compose Kudryavyi Volcano (Fig. 2). Within the limits of error, the Pb isotopic composition of the recent Chernysh basaltic andesite flow is very close to that of other rocks that compose the edifice [3]. The field of experimental points corresponding

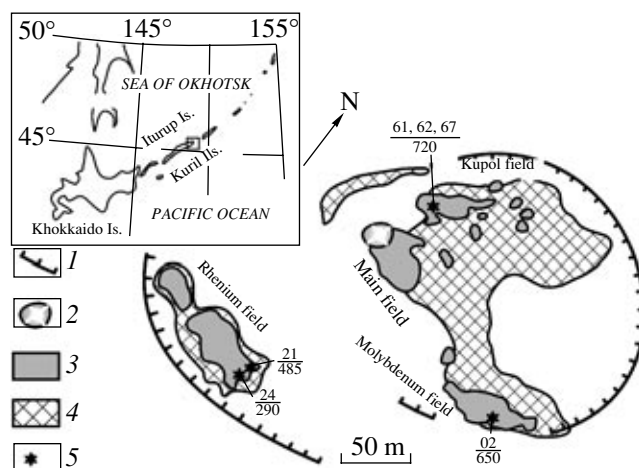


Fig. 1. Location scheme of fumarole fields of Kudryavyi Volcano (Iturup Island, Kuril island arc) with indication of sampling sites (modified after [6]). (1) Boundaries of the Kudryavyi Volcano crater; (2) phreatic crater; (3, 4) fumarole fields: (3) high-temperature (>200°C), (4) low-temperature (<200°C); (5) sampling localities and maximum temperature (°C) of the fumarole channel.

to gas condensates and mineral sublimates overlaps with that of volcanic rocks. This suggests that basaltic andesites and the high-temperature fluid of Kudryavyi Volcano had a common Pb isotope source. Note that the high homogeneity of Pb isotope ratios in the products of high temperature fumarole activity together with similar Pb–Pb isotope characteristics of the fluid and volcanic rocks is also observed in the volcanic–fumarole systems of Tolbachik (Kamchatka) and Vulcano (Italy) [7–9].

The geotectonic setting of the Kuril island arc attests to the two most probable geochemical Pb sources of products of Kudryavyi Volcano activity. One source is the oceanic crust subducted in the Kuril island-arc zone with depleted MORB mantle Pb isotope characteristics. The other geochemical reservoir is bottom oceanic sediments, which also participate in the subduction process. Based on ODP Site 881 drilling data, the thickness of sediments overlying oceanic basalts on the ocean side of the Kuril arc is no more than 500 m [10]. The sedimentary section consists of 164-m-thick Late Pliocene–Pleistocene diatom siliceous clays, which overlie the pure Miocene–Late Pliocene diatomites, which are more than 200 m thick. A similar section was recovered by holes DSDP 579 and 581 [11]. The influence of seawater Pb should be ruled out owing to its negligible content in the oceanic water [12]. The high homogeneity of Pb isotopic composition in the products of fumarole and the magmatic activity of Kudryavyi Volcano rules out the assimilation of Pb by melts from the heterogeneous host island-arc crust in the intermediate volcanic chambers.

In the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ and ^{206}Pb – ^{204}Pb – $^{208}\text{Pb}/^{204}\text{Pb}$ diagrams, the field of Pb isotopic composi-

Pb isotopic composition of gas condensates, ore minerals, and volcanic glass from the basaltic andesite of Kudryavyi Volcano (Iturup Island, Kuril islands)

Sample	T, °C	Material	Pb, µg/kg	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	μ_2
2101	485	Condensate	16	38.24	15.52	18.38	9.3
0202	640	The same	260	38.23	15.51	18.40	9.3
6103-1	720	"	1640	38.04	15.47	18.36	9.1
6103-2	720	"	1070	38.24	15.52	18.40	9.3
0204	620	"	220	38.26	15.52	18.41	9.3
6104	720	"	810	38.26	15.52	18.41	9.3
2104	420	"	104	38.12	15.50	18.30	9.3
2401	290	Cannizzarite		38.28	15.53	18.42	9.4
6202	650	Galena		38.24	15.51	18.40	9.3
6703	620	Cannizzarite		38.27	15.52	18.41	9.4
2403	290	The same		38.30	15.53	18.42	9.4
1-4		Glass, basaltic andesite glass		38.26	15.52	18.40	9.3

tions of sediments and MORB are clustered separately (Fig. 2). The bottom sediments of the Northern Pacific are enriched in ^{207}Pb and ^{208}Pb with respect to MORB-type Pb. Data points of condensates and sublimate min-

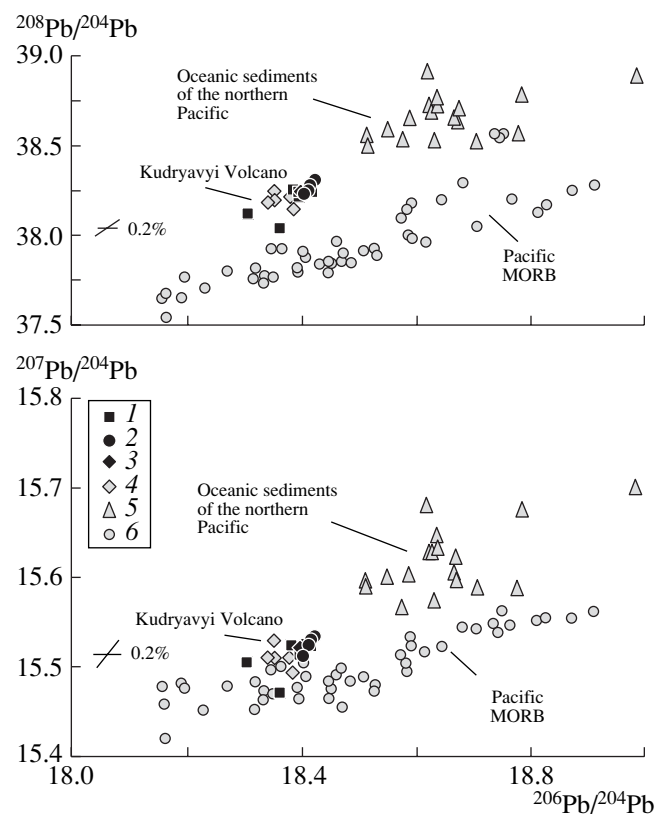


Fig. 2. Pb isotope ratios in (1) condensates of fumarole gases, (2) mineral sublimates, and (3) the Chernysh basaltic andesite flow of Kudryavyi Volcano. Also shown are (4) fields of Pb isotopic composition of the Kudryavyi Volcano lavas ([3]), (5) bottom sediments of the northern part, and (6) the Pacific MORB (after [10]).

erals are plotted near the field of MORB-type Pb, indicating the leading role of this source. At the same time, lavas and high-temperature fluid related to the activity of Kudryavyi Volcano have an elevated content of ^{208}Pb . In our opinion, this testifies to the involvement of Pb from the bottom sediments of the northern Pacific. It is difficult to estimate the amount of sedimentary material delivered to the subduction zone owing to wide variations in the isotopic composition and abundance of Pb in the Pacific bottom sediments. However, as was shown for the Aleutian Island lavas having higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than Kudryavyi Volcano, even an insignificant addition (less than 2%) of oceanic sediments to mantle source leads to a significant shift of the Pb isotopic composition in the volcanic rocks relative to MORB values.

Thus, the Pb–Pb isotope study of condensates of high-temperature fluid and mineral sublimates of the ore-forming system of Kudryavyi Volcano indicates the predominant role of the magmatic source, which has a homogenous Pb composition close to that of the depleted Pacific MORB mantle. However, the elevated content of ^{208}Pb in lavas and fumarole gases relative to the MORB-type Pb source also suggests the contribution of a source with a more radiogenic Pb composition. This source can be bottom sediments of the Pacific Ocean, whose input is of subordinate significance. A homogenous Pb isotopic composition in the source of the high-temperature fluid presumably was attained during deep-seated interaction of the lithosphere and asthenospheric mantle.

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