GEOCHEMICAL VALUE OF AEROSOL TRANSPORT PROCESSES

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Our researches of polyelement emission streams from a soil cover and composition specificity of volcanic aerosols have led us to a conclusion that is geochemistry area practically is not developed in the relation of microelement migration in Earth's spheres: lithosphere – atmosphere. Nanoaerosol particles (0,001 – 1 microns) submit to laws of gas dynamics [13, 40] and in fluid streams are steady enough. Experimental researches of polyelement emission streams from soils [4-7, 41] and low-temperature microelements migration have allowed to detail the reasons of rather high values of the soil emission noted in publications [39, 43, 44, 46-49] of last decade which methodical security raises the doubts. High emission hard-volatile macro-and the microcomponents, received by a method of cryogenic traps and published [39, 43, 44] (0.01-10 mg/m^2·day on summary mineral emission) estimations lead this process in one of the important receipts in total balance of the atmosphere [17-20], comparable with aerosol dust contamination. Complexity of authentic definition of forms [32, 33], structure and dispersion of particles of the gas phase emitting from a soil cover, is substantially connected with absence of methodically proved receptions of selection of condensates [9, 10], free from aerosol components, and methods of their reliable division in a stationary stage of process [25-27]. Reception of the new information on factors of distribution of metals between pore solutions, true gas complexes and mineral phases of soils, an estimation of a role gas electrophoresis at transition to molecular cluster [16] and to water colloid [13, 40] aerosols (0.1 microns and less) have allowed us to clear up estimations of streams of soil emission.

In the world geochemical literature till 80th years of the twentieth century was very little given on metal-bearing high-temperature volcanic gases. Powerful Tolbachinsky eruption (PTE) 1975 - 76 has allowed to select tests of condensates at temperatures to 1000 degrees and to receive reliable quantitative definitions of maintenances in them of the big number of chemical elements, including Zn, Cu, Pb, Au, Ag, Pt. Practically for the first time scales of carrying out of elements volcanic exgalations - derivatives the magnesia basalts melt arriving on a surface with the big speed from area of the top cloak [24] have been defined. The differentiation of a multicomponent gas phase in near surface conditions crater zones on Northern break PTE, caused by various solubility of flying compound in silicate melt, distinctions in their temperatures of boiling, thermodynamic stability, and also in elasticity of steams of gas complexes, leads concentration certain compound of elements and to formation ore-bearing bed to copper, zinc and other metals. In structure exgalation ore minerals many native metals - gold, silver, copper, lead, bismuth, tungsten, numerous intermetallic compound have been noted: sulphates, oxisulphates, chlorides and oxichlorides Cu, Zn, Pb, Fe, Al, V, Te, Se, Bi, oxides iron and copper [12, 14, 15, 28, 29]. Gold formation has been fixed in the range of temperatures 180-625 ºC. It meets in the form of individual crystals with hexagon contours, trapezes and triangles or insignificant congestions of crystals fine-lamellate, needle, to hair-like habitus. The sizes of individuals of gold vary from 250 x 50 x 10 microns to 0,3 mm in a diameter, at a thickness of an order of 0,01-0,005 mm. Classical forms of fast growth of individuals from a gas phase were marked. The proof of realisation of carrying over of ore components modern magmatic fluid systems is also detection of the big number of ore formations in ashes active volcanoes. So, we find out numerous grains of native metals - Fe, Al, Zn, Cu, iron oxides [21, 22] in eruption ashes volcanoes of Kamchatka - Karymsky, Anonymous, Kljuchevsky and Shiveluch [22], and recently also sulphides of iron and intermetallic compounds Fe, Ni, Cr, Mo, Mn. Grains of native metals are usually presented by the isolated units of the same size combined from nanosize particles of an order of 0.2 microns. For oxides and sulphides of iron, and also often enough meeting individuals of native iron and glass most typical globular form of formations which can be caused vortical conditions in a zone of transport and fine-dispersed state of the high-temperature fused magmatic substance sated with gases. Geochemical specificity of aerosol carrying over in eruption columns at eruptions, often consists in high cleanliness individual выделений native metals from typical elements - impurity. Presence of W without Mo and similar examples for other metals force to assume presence of the specific gas complexes which stability is rather various at sharp changes of pressure and temperatures in eruption columns at eruptions. Our analysis has shown, that for a role of such forms of carrying over can apply metals carbonyls, widely

used at reception of especially pure substances. These covalent compounds with formally 0-valency Me in a complex kernel contain variable quantity of groups CO in ligand parts and always complete the electronic cover [31] to a cover of following inert gas, i.e. have in external sphere 4, 5, 6 groups CO, that together with the big distinctions in dependences of constants of formation on temperature their disintegration does non-simultaneous. Calculations show, that at andesite eruptions on oxygen buffers QFM and Ni/NiO, at any molar parts of carbonic acid in a gas phase, all carbon oxide can be connected in carbonyl complexes, appearing in a free condition only in process decompression. Earlier [1-3, 45] we have shown, that solubility hard volatile components in fluids of low density is connected not with their own volatility, but with association reactions, complexation and solvation with more flying gas components. In the given research the approach develops also on properties of more difficult real forms of carrying over - gas clusters and nanosize aerosols which, submitting to laws of gas dynamics, are capable to issue from soils and thermal waters, especially, in electric field of circumterraneous atmosphere (gas electrophoresis). Are designed, made and used at carrying out of field both laboratory experiments refrigerating and cryogenic installations for studying of microelement emission from soils different climatic regions of Russia. For the first time selection of condensates us is executed from various horizons of soil cuts for definition of depths and mechanisms of receipt of various components in condensates. The methods earlier developed by authors, it is carried out not only selection of condensates, but also gaseous-aerosol phases in the conditions of them convection migration with structure fixing on acid and alkaline bubblers. The developed methods of selection of soil aerosol condensates in experiments with domination diffusion or convection mass transfer has shown the leading part of conditions of hashing in concentration dependences and defining role of hydration by water steams, and also natural electric fields, in formation of associations of the main elements and microelements. These approaches are transferred now by us on fumarol and volcanic aerosols. Application of methods ISP-MS of analyses and an ultrafiltration allows to receive factors of distribution for a wide set of elements of phases of aerosols and between initial gas, a liquid and organomineral phases of soils.

We believe, that aerosol carrying over steady gas clusters less than 1 microns when to them the equations of gas dynamics are applicable and is observed by the size Brown movement without sedimentation - absolutely real and important phenomenon of fluid carrying over of components in various geochemical conditions. Transition – from simple gas forms through gas polymeric complexes to permolecular clusters and to aerosols, - is continuous, but the thermodynamic description of structure gas clusters and aerosols should be spent in terms of thermodynamics of small ensembles, - such objects as volume fragments of a liquid or firm phase are unpresentable statistically. The dualism of formations is fixed last decades in terms of type "geogas" and to it similar [46-49]. Results under maintenances of mercury and issue of its mononuclear steams, including, in gaseous-hydrothermal systems of Kamchatka (volc. Mutnovsky, volc. Karymsky, volc. Uzon, Apapelsky sources), also show relevancy of the contribution to carrying over of mercury of gaseous-steam aerosols [34-36]. So, for mercury thermodisplays of Apapel stream [42] in a gaseous-steam phase it is direct on sources concentration we are found: 9500, 190000 and 311000 ng/m^3, that will well be correlated with Ozerova's data with co-authors [30]. According to Ozerova the highest maintenance of mercury in the gas phase, fixed on an exit of Apapelsky sources, 75000 ng/m^3, that on three order above the value measured by them in atmospheric air of sampling area. This result is, on the one hand, in the consent with our data, but in the obvious contradiction with the size of a constant of Henry defined in work [38] and our data under total maintenances of mercury in thermal waters of Kamchatka [8, 27], varying in the range of 0.14 - 2.3 ppb at often obvious prevalence of the oxidised forms of mercury. For check and the coordination of results of these works was carried out thermal waters sampling of Apapelsky sources and also concentrations of mercury in gaseous-steam phase was determined by atomic absorption spectrometry using Universal Complex Mercury Measuring UCM-1MC and in the sample selected in bubbler with 3 % HNO_3 after preliminary condensation of a steam phase. Last value (72 ng/m^3 gaseous-steam phases) will well be co-ordinated with the mercury concentration on a gold sorbent (92 ng/m^3) and characterises zero-valency the carrying over form.

Table 1

Mercury concentrations in sources and steam condensates Apapelsky "upper" sources

Source	Sample	Source characteristic	Hg in water, ppb	Hg, ng/m^3,air-water aerosol condensate
APV-05	КМЧ-109/07	t=84,7 ^{0}C, s=1068 mg/l (by NaCl), pH = 7,8, Eh = 545 mV	0.194	9500
APV-09	КМЧ-113/07	t=64,1 ^{0}C, s=536 mg/l (by NaCl), pH = 7,9, Eh = 379 mV	0.481	190000
APV-13	КМЧ-110/07	t=97,6 ^{0}C, s=1189 mg/l (by NaCl), pH = 8,8, Eh = 589 mV	0.189	-
APV-14	КМЧ-111/07	t=88 ^{0}C, s=1002 mg/l (by NaCl). pH = 7,2, Eh = 367 mV	0.227	311000
APV-19	КМЧ-114/07	pH = 7,18, Eh = =400,00	0.242	-

Apapelsky "lower" sources

Source	Sample	Source characteristic	Hg in water, ppb	Hg, ng/m^3, water aerosol conden-sate
Source №1	КМЧ-103/07	t=41,7 ^{0}C , s=586 mg/l (by NaCl), pH = 7,3, Eh = 310 mV	0.188	-
Source №2 (bath), first sink	КМЧ-104/07	t=41,5 ^{0}C, s=1024 mg/l (by NaCl), pH = 8,4, Eh = 329 mV	0.177	-
Source №2 (bath), second sink	КМЧ-105/07	t=52,2 ^{0}C, s=1041 mg/l (by NaCl), pH = 6,75, Eh = 347 mV	0.296	2680
Bath with two gryphons SW sources	КМЧ-106/07	t=25,7 ^{0}C, s=738 mg/l (by NaCl), pH = 6,8, Eh = 366 mV	0.177	-
"Kanavnye" sources	КМЧ-107/07	t=81 – 81,5 ^{0}C, s=1170 mg/l (by NaCl), pH = 7,3, Eh = 445 mV	0.487	7350

These values are in sharp contrast with data under the total maintenance in condensates of a steam phase according to Ozerova with co-workers [30] and to ours (tabl. 1). High values of mercury concentrations in condensates (3.3 – 124 ppb, at recalculation volume concentration of mercury in air on weight of a condensate, taking into account pressure of sated water steams last column of tabl. 1) are in the obvious contradiction with concentration of mercury in water a term and can be explained considerable carrying over to an aerosol phase.

In Ozerova's work, etc. [30]. High mercury concentrations in condensates gaseous-steam phases of modern thermal sources that testifies, according to authors, to receipt mantle mercury on zones of the deep breaks, proceeding and are noticed now. So, data cited by authors about mercury concentrations in a gas phase of thermal sources Uzon caldera, vary from 1 to 2 g/m^3 (2.5 - 60 ppb, i.e. 2.5 - 60 mkg/l of a condensate of water steam in density 0.4 g/l). The highest mercury concentrations are noted by authors at selection of condensates gaseous-steam streams from a volcano crater Mutnovsky, - they made 5-7 g/l (50-75 mkg/l, ppb), reaching very high concentration 2*10-3 g/l a condensate, that authors contacts eruption of a volcano Gorely. It is necessary to notice, that such concentration (from 2.5 to 5000 ppb) for a condensate 85-100^o - steam actually are unique and answer the periods of activization of volcanic and fluid activity. The exception is represented by system Uzon caldera for which till the present period high concentration of mercury are stable enough not only in a gaseous-steam phase, but also in chloride-natrium waters [28], reaching (according to VSEGINGEO) 2 ppb. But, at the same time, on our data [8] for operational chinks GeoES in Mutnovsky geothermal system in condensates

and separates concentrations 0.2 - 0,5 ppb, and for other geothermal systems frequently [23] are usual and a little higher, but in norm in waters seldom above 1 ppb. It is in the consent with results of last our definitions of the maintenance of mercury resulted here in water of Apapelsky sources and well confirms the early version [38] about domination in gaseous-steam phase the atomic mercury, slow accumulation of its oxidised forms [37] in solutions and transition in sulphidic phases at a certain mode of hydrogen sulphide and polysulfans [11, 45]. To co-ordinate these inconsistent data on rather low concentration in a liquid phase and to high concentration in gaseous-steam phase it is possible in the prevalence version zero-valent and cationic complex mercury forms in an aerosol phase.

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