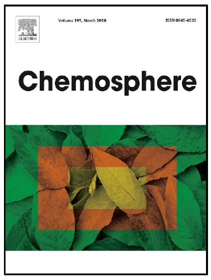

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Nanoparticles of volcanic ash as a carrier for toxic elements on the global scale

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Abstract

At present, there is concern about engineered nanoparticles in the environment, whereas natural nanoparticles (NPs) and their impact are often neglected. In our paper, we demonstrate the important role of nanoparticles of volcanic ash in transport of toxic elements on a global scale. A single volcanic eruption can eject millions of tons of ash. NPs of volcanic ash reach the upper troposphere and the stratosphere and may "travel" around the world for years affecting human health, environment, and even climate. So far, there is a gap in exposure assessment of volcanic ash NPs since their chemical composition remains largely unknown. Here we show for the first time that volcanic ash NPs can serve as an important carrier for potentially toxic elements. The concentrations of Ni, Zn, Cd, Ag, Sn, Se, Te, Hg, Tl, Pb, Bi in volcanic ash NPs (<100 nm) were found to be 10-500 times higher than total contents of these elements in bulk samples. This is valid for volcanoes from different regions of the world (Kamchatka, Far East of Russia and Andes, Chile). The work opens a new door into studies on biogeochemical impact of volcanic ash.

Keywords: volcanic ash, nanoparticles, toxic elements, natural hazard

1. Introduction

Specific properties of nanoparticles (NPs) and related risk assessment require special attention [1-3]. Recent studies are mainly focused on engineered nanoparticles [4-7]. It seems unfair taking into consideration that about 90% of aerosol NPs in the environment are of natural origin [8]. Natural NPs coming from volcanic eruptions, soil erosion, and dust storms surround humanity from time immemorial [9]. During one eruption upwards of 30 million tons of ash, can be ejected to the height of tens of kilometers and reach the stratosphere, where volcanic ash NPs may spread worldwide and affect all areas of the Earth for years [8]. It is known that the periods of active volcanism on our planet coincide with its global cooling [10, 11], which was caused by the absorption and scattering of solar radiation by airborne volcanic ash particles [12]. Volcanic ash as a source of nutrient elements (e.g. iron and phosphorus) can increase bioproductivity of phytoplankton [13-16] and affect the global balance of CO_2 [17, 18]. Along with nutrient elements, volcanic ash contains toxic metals and metalloids. Since NPs of volcanic ash are extremely mobile in the environment and have an increased ability to penetrate into living organisms (e.g. by inhalation, ingestion, through the skin) [9], their investigation is of importance to environmental geochemistry. Besides, understanding geochemical reactions and processes at nanometer scales, especially with regard to the formation of nanostructures in geological materials, the emergent properties of these structures, and their impact to geochemical processes is one of the main challenges of nanogeochemistry [19].

However, despite the rapid development of analytical instrumentation and corresponding methodologies, there is a gap in studies on chemical composition of natural NPs and their fate in the environment. The main reason is the difficulty to recover NPs from environmental samples for further characterization and quantitative analysis. In fact, NPs in polydisperse environmental samples such as dust, volcanic ash, or soil may represent only one thousandth or less of the bulk sample [20]. Therefore, the recovery of NPs followed by quantitative analysis is a complex task.

The present work aims to investigate chemical composition of NPs of volcanic ash from different regions of the world and to evaluate the potential hazard of NPs as a carrier for toxic elements on global scale.

2. Materials and Methods

2.1 Samples of volcanic ash

Ash samples of volcanoes Tolbachik, Klyuchevskoy (Kamchatka, Russia, eruptions of 2012 and 2015, correspondingly), and Puyehue (Puyehue-Cordón Caulle volcanic complex, Andes, Chile, eruption of 2011) were under study. Klyuchevskoy and Puyehue are stratovolcanoes, therefore, content of ash may attain one third of the total ejected mass. It should be noted that Klyuchevskoy is among the most productive arc volcanoes on Earth [21, 22]. Tolbachik is a predominantly basaltic volcanic complex in the Central Kamchatka depression and belongs to the Klyuchevskoy volcanic group. However, Tolbachik is a volcano formed by lava flows (so called Hawaiian type) and content of its ash is less than 1% of the total mass ejected during the eruption. Puyehue ash sample (about 2 kg) was collected in June, 2011 immediately after eruption of volcano and put into a polyethylene bag. Ash samples of Klyuchevskoy and Tolbachik volcanoes were collected during winter season after eruptions from the snow surface and put into polyethylene bags. The weight of each ash sample was not less than 1 kg. After melting the ash-snow mixture, the ashes were dried at 25°C in a well-ventilated room.

2.2 Separation and characterization of volcanic ash nanoparticles

The separation of nanoparticles from volcanic ash samples was performed on a planetary centrifuge with a vertical single-layer coiled column according to previously developed methodology [23, 24]. The scheme of planetary motion of the rotating coiled column is presented in Fig. 1A. The solid sample (1 g) was introduced into the column (filled with deionized water) as a suspension in 10 mL of water. Then, the column was rotated at 800 rpm and water was continuously fed into the column. The separation of nanoparticles was achieved at a flow rate of 0.7 mL min^{-1}. The basic principle of the separation process of NPs in the rotating coiled column is shown in Fig. 1B. The particulate matter in the column effluent was monitored using a flow spectrophotometer.

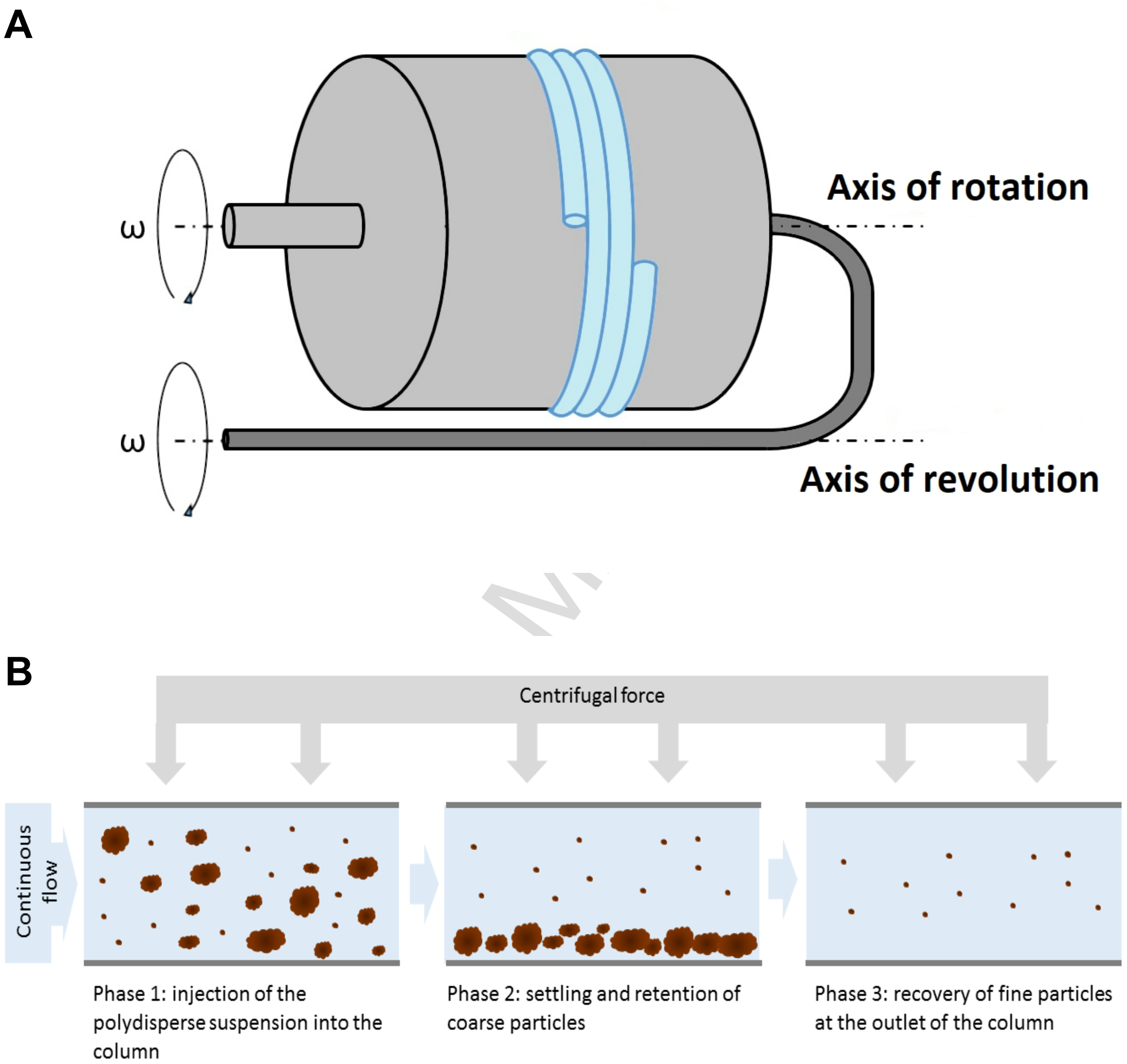

Figure 1. The scheme of planetary motion of the rotating coiled column (A) and the basic principle of the separation process of NPs in the rotating coiled column (B).

The separated fractions of nanoparticles were characterized by scanning electron microscopy (Tescan MiraLMU, Czech Republic) and laser diffraction method (Shimadzu SALD-7500nano, Japan). Nanoparticles were precipitated on membrane filters (20 kDa) under pressure of 3 bars using a filtration cell. Then, the filters were digested and analysed by ICP-AES and ICP-MS techniques.

2.3 Digestion and analysis of volcanic ash samples and their nanoparticle fractions

Samples of the volcanic ash as well as standard geological samples (*Gabbro GSO 521-84P* (Russian Standard Sample), *Andesite, AGV-2* (United States Geological Survey) and *Granodiorite, Silver Plume, Colorado, GSP-2* (United States Geological Survey)) were digested in both autoclave and open beaker using a combination of acids.

For the digestion in open system, the particulate samples (0.1 g) were put into 50 mL Teflon beakers together with 0.5 mL $HClO_4$ (Perchloric acid fuming 70% Suprapur, Merck), 3 mL HF (Hydrofluoric acid 40% GR, ISO, Merck), 0.5 mL HNO_3 (Nitric acid 65%, max. 0.0000005% Hg, GR, ISO, Merck), and 0.1 mL of solution containing 6-8 ppb ^{62}Ni, ^{76}Se, ^{149}Nd, ^{161}Dy, and ^{174}Yb isotopes which were necessary to control completeness of digestion [25]. The samples with acids were boiled until intensive white fumes appeared. Then the beakers were cooled, 3 mL deionized water was added to each of the beakers, and the samples were boiled down once again. After this, 2 mL HCl (Hydrochloric acid fuming 37% GR, ISO, Merck) and 0.2 mL 0.1M H_3BO_3 solution were added to each sample, and they were boiled down to approximately 0.6 mL each. Then the samples were transferred to polyethylene beakers, diluted to 20 mL with deionized water, and 0.1 mL of 10 ppm In solution was added to each sample as an internal standard. For control, all the described procedures were also performed in three empty beakers.

For the digestion in autoclave, the samples were put into Teflon beakers together with 2 mL HF and 0.5 mL HNO_3, and 0.05 mL of solution containing 8 mg L^{-1} ^{146}Nd, 5 mg L^{-1} ^{161}Dy, and 3 mg L^{-1} ^{174}Yb, covered with caps and stored for 6-8 hours at room temperature. Then, the beakers were opened and boiled down at 170-180°C. After cooling, 2 mL HF, 0.5 mL $HClO_4$, and 0.2 mL HNO 3 were added to each sample, the beakers were closed and placed in the autoclave titanium housings. The autoclaves were put in an electric furnace and held at 160°C (1 h), 180°C (1 h), 200°C (1 h) and 220°C (0.5 h). After cooling, the samples were boiled down at 170-180°C. Then, 1 mL HCl and 1 mL HNO_3 were added to each of the sample, the beakers were closed and held for 1 h at 160°C. After the autoclaves were cooled down, they were opened and the solution was evaporated to dryness. Then, 1 mL HCl and 1 mL HNO_3 were again added to the beakers and the steps of heating at 160°C and evaporation to dryness were repeated. The dry residue was dissolved in 0.8 mL HCl and 0.8 mL HNO_3 at 80-100°C heating and transferred to polyethylene test tubes, the solution volume was brought up to 10 mL with deionized water. The solutions from the beakers without analyzed sample were used as control ones. Before measurements all the solutions were diluted by 5 times and an internal standard of 10 μg/L In was added.

The digestion of the filters were performed in a mixture of 0.5 mL HNO_3 and 1.0 mL HCl using an autoclave system at 160°C (1 h), 180°C (1 h) and finally 200°C (1 h).

The contents of B, Li, Be, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U in the samples were determined using an ICP-MS (X-7, Thermo Scientific, USA). The measurements were made using the following parameters: a RF generator power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 13 L min^{-1}; an auxiliary Ar flow rate of 0.9 L min^{-1}; an Ar flow rate into the nebulizer of 0.9 L min^{-1}; an analyzed sample flow rate of 0.8 mL min^{-1}. The contents of Li, B, Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, and Ba were determined by ICP-AES (iCAP-6500 Duo, Thermo Scientific, United States, USA). The measurements were made using the following parameters: a RF generator power of 1200 W; a VeeSpray nebulizer; a plasma-forming Ar flow rate of 12 L min^{-1}; an auxiliary Ar flow rate of 0.5 L min^{-1}; an Ar flow rate into the nebulizer of 0.6 L min^{-1}; an analyzed sample flow rate of 1.8 mL min^{-1}. For elements, which were determined both by ICP-AES and ICP-MS, average values were used. It should be noted that the data for these elements confirmed the accuracy of the results obtained by both methods. The results obtained for standard samples are in good agreement with the certified values.

3. Results and Discussion

3.1 Chemical composition of volcanic ashes

The determined total concentrations of representative trace elements (including toxic and potentially toxic ones) in volcanic ash samples (Table 1) do not exceed their average contents in the Earth crust [26]. The concentrations of copper in Tolbachik ash (about 250 ppm) and selenium in Puyehue ash (1.6 ppm) can be noted as an exception. Hence, it has been demonstrated that bulk samples of volcanic ashes under study are not enriched by any toxic elements.

3.2 Separation, characterization and analysis of volcanic ash nanoparticles

As has already been mentioned, the investigation of chemical composition of natural nanoparticles is limited by difficulties of their separation from bulk sample and subsequent quantitative analysis. The authors have suggested to solve this problem using their original combined analytical approach, which is based on the separation of nanoparticles by sedimentation field-flow fractionation in a rotating coiled column, characterization of their size and morphology, elemental analysis, and calculation of the obtained results. In the present study this approach has been further developed and applied to studies of volcanic ash samples from different regions of the world.

Table 1. Concentration of representative major and trace elements in bulk samples and nanoparticle fractions of volcanic ashes (n=4, P=0.95)

Element	Earth's crust	Tolbachik		Klyuchevskoy		Puyehue	
		Bulk	**Nanoparticles**	**Bulk**	**Nanoparticles**	**Bulk**	**Nanoparticles**
				%			
Na	2.4	2.8	1.0 ± 0.3	2.4	2.3 ± 0.3	3.6	3.1 ± 0.3
Al	8.2	8.4	6.5 ± 2.5	8.6	11.8 ± 0.9	7.4	8.3 ± 0.1
Si	28.2	-	20.6 ± 2.4	-	21.6 ± 1.8	-	29.6 ± 2.1
K	2.1	2.0	0.6 ± 0.1	0.8	0.5 ± 0.2	2.3	1.3 ± 0.1
Ca	4.2	5.1	2.8 ± 1.0	5.7	6.3 ± 0.9	1.6	4.9 ± 3.0
Fe	5.6	6.9	20.0 ± 6.0	6.2	10.1 ± 0.8	2.9	3.9 ± 0.3
				ppm			
Ni	75	9	$(0.28 \pm 0.03)\times10^3$	22	< 26	0.7	49 ± 6
Cu	55	0.24×10^3	$(2.4 \pm 0.4)\times10^3$	68	$(0.92 \pm 0.06)\times10^3$	16.4	< 47
As	1.8	3.4	$(0.7 \pm 0.1)\times10^3$	0.6	< 2	4.0	< 17
Se	0.05	< 2.5	$(0.3 \pm 0.1)\times10^3$	< 0.7	< 34	1.6	< 60
Ag	0.07	0.10	6.4 ± 1.2	0.07	3.1 ± 0.8	0.1	6 ± 4
Cd	0.2	< 0.03	1.7 ± 0.8	0.1	3.3 ± 0.8	0.1	2.7 ± 0.6
Sn	2	1.6	65 ± 15	0.9	38 ± 9	2.6	29 ± 5
Te	-	< 0.05	27 ± 9	< 0.05	9.3 ± 3.6	< 0.07	<1.6
Hg	0.08	0.07	29 ± 7	0.08	36 ± 4	< 0.08	9 ± 7
Tl	0.45	0.19	19 ± 3	0.08	7 ± 1	0.5	11 ± 1
Pb	12.5	7	$(0.24 \pm 0.04)\times10^3$	3	62 ± 12	23	$(0.16 \pm 0.03)\times10^3$
Bi	0.17	0.10	35 ± 10	0.06	6.1 ± 0.4	0.22	35 ± 6
La	30	21	38 ± 7	7	13 ± 4	29	40 ± 2
Ce	60	51	95 ± 17	18	31 ± 10	66	84 ± 4
Pr	8.2	7.5	14 ± 2	2.8	4.5 ± 1.3	8.6	11 ± 1
Nd	28	33	63 ± 8	13	22 ± 4	37	48 ± 4
Y	33	40	51 ± 9	22	27 ± 3	53	59 ± 2
Gd	5.4	7.7	12 ± 2	3.9	6 ± 1	8.6	10 ± 1
Dy	3.0	7.2	10 ± 2	4.0	5.4 ± 0.4	8.8	10.4 ± 0.4
Ho	1.2	1.5	2.0 ± 0.3	0.9	1.1 ± 0.1	1.8	2.1 ± 0.1
Th	9.6	3.2	8 ± 1	0.6	1.5 ± 0.3	8.6	15 ± 2
U	2.7	1.7	1.8 ± 0.3	0.5	0.9 ± 0.1	2.3	3.3 ± 0.2

The separated nanoparticles of volcanic ash were characterized by laser diffraction (Fig. 2). As is seen form the light scattering data, the average particle sizes in obtained fractions are 91, 54, and 34 nm for Tolbachik, Klyuchevskoy, and Puyehue ashes, correspondingly. Since the same methodology was applied to the isolation of nanoparticles from all three samples, the difference in their size distributions is evidently caused by specific characteristics of the eruptions. Laser diffraction is an indirect method of measuring the particle size and the data were confirmed by scanning electron microscopy. The micrographs of separated nanoparticles of volcanic ash are shown in Fig. 3. In general, nanoparticles have a spherical or ellipsoidal shape with a smooth surface. This is evidently the result of high temperature processes occurred during eruptions. Slightly increased size of Tolbachik nanoparticles may be attributed to agglomeration of nanoparticles, which may be observed on the corresponding micrograph.

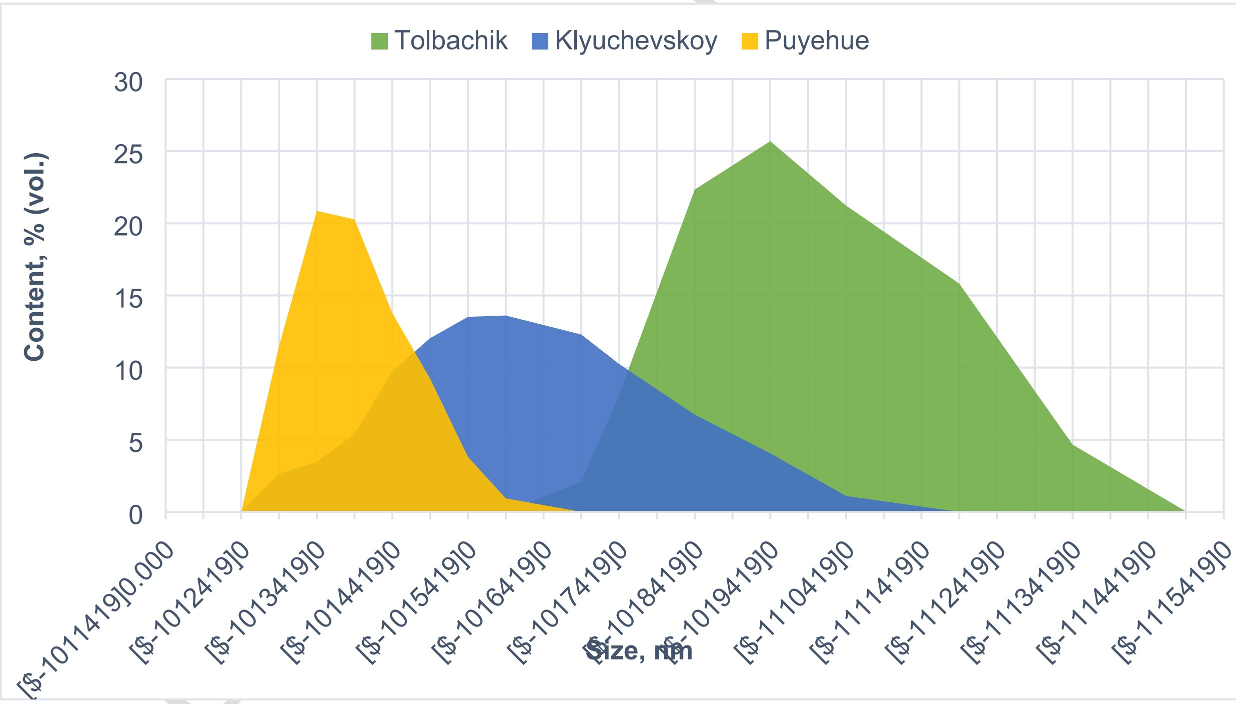

Figure 2. Size distribution of separated volcanic ash nanoparticles as obtained by laser diffraction. The comparison of particle size distributions for nanoparticle fractions of ashes of Tolbachik, Klyuchevskoy, and Puyehue volcanoes.

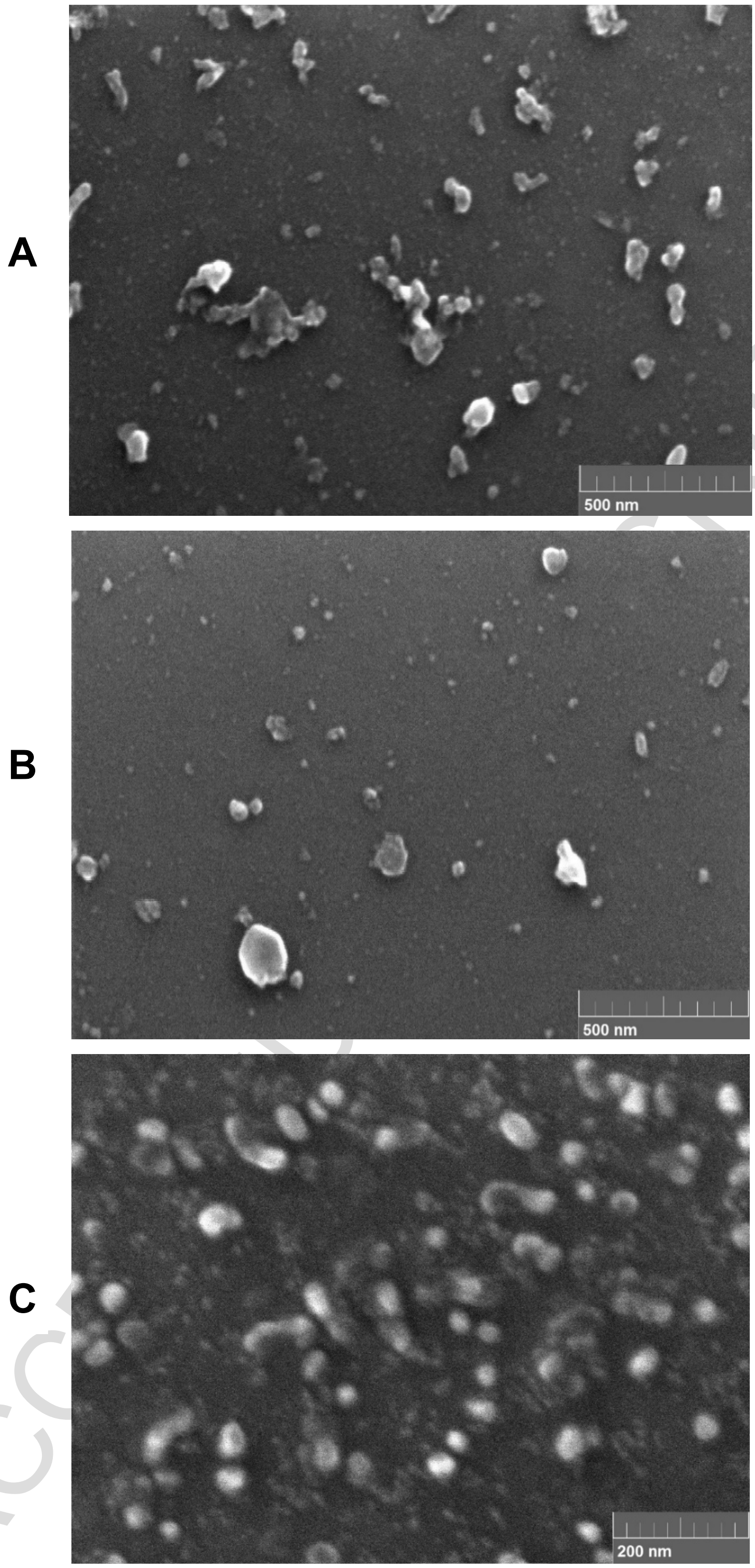

Figure 3. Micrographs of volcanic ash nanoparticles. Characterization of size and morphology of ash nanoparticles of Tolbachik (**A**), Klyuchevskoy (**B**), and Puyehue (**C**) volcanoes. Nanoparticles have a spherical or ellipsoidal shape with smooth surface. Slight agglomeration of Tolbachik nanoparticles is revealed.

The problem of quantitative analysis of nanoparticles is related to difficulties of precise measurement of their weight after separation. We used another approach to the calculation of element concentrations in volcanic ash nanoparticles. The determined absolute amounts of major elements (e.g. Si, Al, Fe, Ca, etc.) were recalculated to their oxides and the total amount of oxides was considered as the weight of the nanoparticle fraction. The validity of this approach was confirmed using the bulk samples of ash. The calculated concentrations of representative trace elements in volcanic ash nanoparticles are given in Table 1. As is seen, the concentrations of toxic metals and metalloids (Ni, Cu, As, Se, Ag, Cd, Sn, Te, Hg, Tl, Pb, Bi) in volcanic ash nanoparticles are dramatically higher than their bulk concentrations. The reliability of obtained results is confirmed by their good reproducibility. The enrichment factor (EF) for these elements, calculated as

$$EF = \frac{C_{Element}(nanoparticles)}{C_{Element}(bulk\ sample)}$$

is presented in Fig. 4A. Enrichment factors for toxic and potentially toxic elements (Ni, Cu, As, Se, Ag, Cd, Sn, Te, Hg, Tl, Pb, Bi) are in the range from 10 to 500. Elements such as As, Se, Te, Hg, and Bi have the highest EF (at the level of hundreds). High EF (up to one hundred, depending on sample and element) were also found for Ni, Ag, Cd, Sn, Tl, Pb. It should be noted that As and Se were determined only in Tolbachik ash NPs.

Along with the aforementioned toxic and potentially toxic metals and metalloids, the concentrations of rare earth elements (REE), uranium, and thorium in nanoparticles of volcanic ash were also studied (Table 1). The EF of these elements for volcanic ash NPs are also presented in Fig. 4B. In contrast to toxic elements, EF of REE varies from about 1 to 2 for NPs under investigation. The EF of uranium and thorium for nanoparticles are also 1.5 and 2.0, respectively. In general, it has been demonstrated that volcanic ash NPs are not enriched by REE, uranium, and thorium (as compared to toxic metals and metalloids) and their concentrations in NPs are comparable with bulk ones. Since the concentrations of all elements were calculated using a uniform approach, REE as well as uranium and thorium may be considered as elements, which confirm the reliability of the results (i.e. concentrations and EF) for toxic and potentially toxic metals and metalloids.

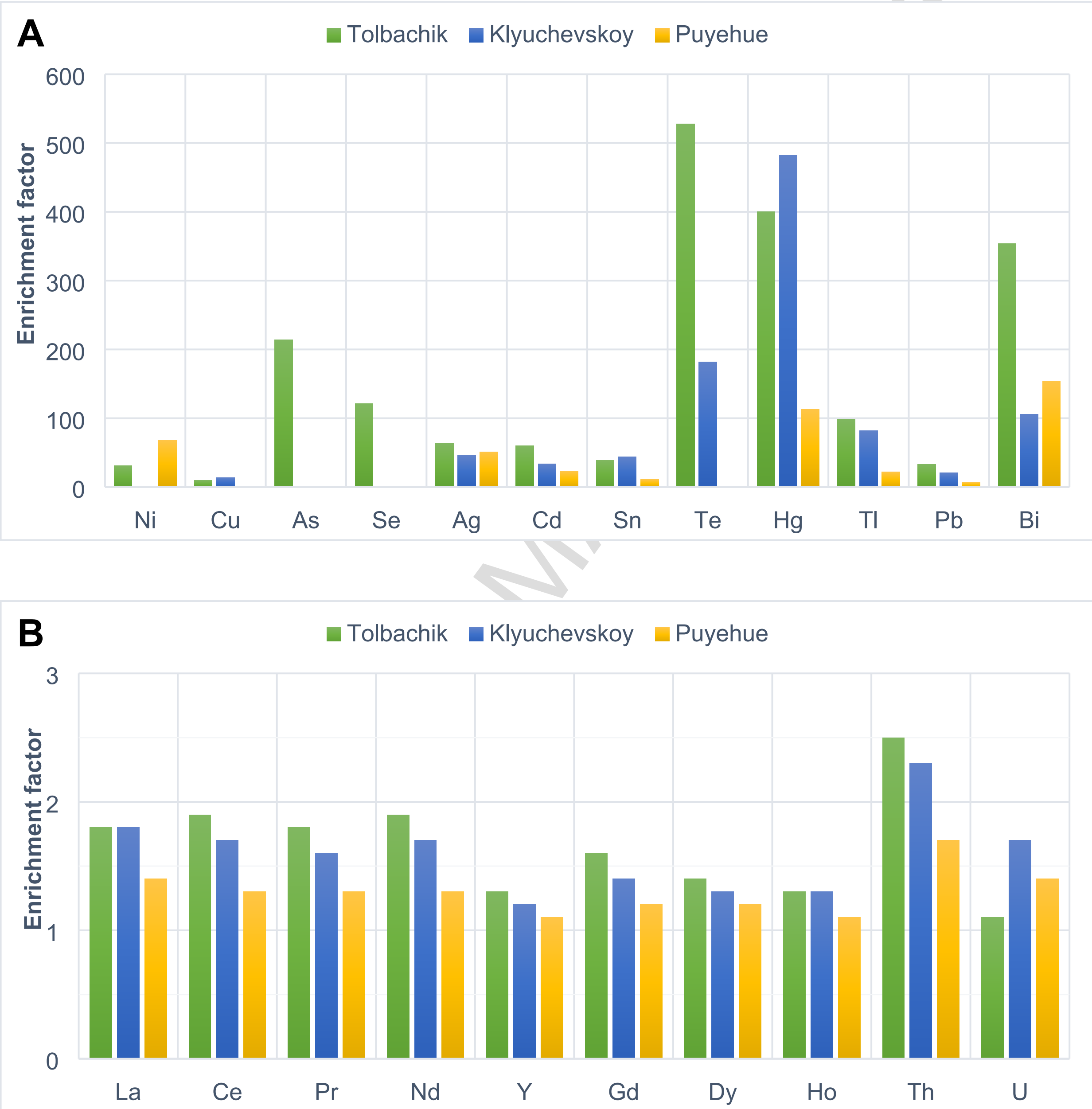

Figure 4. Enrichment factors of representative elements in nanoparticles. Enrichment factors of potentially toxic metalband elements (**A**) and rare earth elements, thorium and uranium (**B**) relative to the bulk concentrations.

3.3 Accumulation of toxic elements by nanoparticles of volcanic ash

It is known that volcanic gases contain a lot of trace elements, for instance Ni, Zn, Cu, Se, Te, As, Pb, Sn, Sb, Ag are among the most mentioned [27-29]. We assume that these elements are accumulated by volcanic ash NPs in the course of eruption. Two processes governing this phenomenon may be suggested: sorption and/or desublimation (gas-to-solid transition).

The extreme specific surface and reactivity of NPs cause their high sorption capability. In this sense, volcanic ash NPs are able to adsorb elements from gaseous phase inside the volcano. Taking into consideration the "extreme" conditions of interaction of volcanic ash NPs and volcanic gases (high temperature and pressure), it can be suggested that the process of *chemisorption* is more probable in this case. On the other hand, the temperature drop in the plume on the outlet of the crater may result in the deposition (desublimation) of elements from gaseous phase, while volcanic ash NPs may serve as a nucleus for this process.

Uneven distribution of EF for different trace elements can be explained by their physical properties, namely, volatility. For elements under study the boiling points increase in the following order: Hg < As < Se < Cd < Te < Tl < Bi < Pb < Ag < Cu < Dy < Sn < Ho < Ni < Nd < Gd < Y < Ce < La < Pr < U < Th [30]. High temperature processes during volcanic eruption lead to the vaporization of some elements that assists their pre-concentration by NPs. The comparison of EF and boiling points showed that the elements with the lowest boiling points have the highest EF, and vice versa. For example, Hg, Te, As, Se with relatively low boiling points in the range 350-1000°C are characterized by EFs of a few hundreds (see Fig. 4). In turn, the absence of accumulation of REE, uranium, and thorium by volcanic ash NPs may be attributed to their high boiling points (about 3000-3500°C for REE and more than 4000°C for uranium and thorium). Of course, it is evident that the chemical composition of volcanic gases is a specific characteristic of individual eruption and cannot be described only from the standpoint of physical properties (e.g. boiling point) of elements.

4. Conclusions

The results obtained in the present research are promising and may have very wide application prospects. Firstly, the capability of volcanic ash NPs to accumulate toxic elements forces the reassessment of their potential biogeochemical impact and health risks. Taking into account the amounts of ejected ash NPs and their high mobility in the environment, the problem is of global scale.

Secondly, some benefits in volcanological studies may also be obtained. The composition of volcanic gases is one of the keys to understanding of processes taking place during eruption. Volcanic gases transport almost the complete Periodic Table. However, most elements have extremely low concentrations (ppb-to–ppm level) [28]. Moreover, the direct sampling of volcanic gases is difficult and only possible in rare cases during effusive eruptions [28]. Due to the accumulation of trace elements from volcanic gases by volcanic ash NPs, their chemical composition indirectly reflects the composition of volcanic gases and thereby may help the study of processes inside the volcano.

Finally, it becomes clear that studies on the fate and behavior of engineered nanoparticles in the environment as well as problems of "nanosafety" should not be separated from in-depth investigation of natural nanoparticles, which are extremely widespread in the environment.

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References

1. Bakshi S, He ZL, Harris WG (2015) Natural nanoparticles: Implications for environment and human health. *Crit Rev Environ Sci Technol* 45(8):861–904. DOI: 10.1080/10643389.2014.921975

2. Nowack B, Bucheli TD (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut* 150(1):5–22. DOI: 10.1016/j.envpol.2007.06.006

3. Biswas P, Wu CY (2005) Nanoparticles and the environment. *J Air Waste Manage Assoc* 55(6):708–746. DOI: 10.1080/10473289.2005.10464656

4. Bhatt I, Tripathi BN (2011) Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment. *Chemosphere* 82(3):308–17. DOI: 10.1016/j.chemosphere.2010.10.011

5. Tiede K, Boxall AB, Tear SP, Lewis J, David H, Hassellov M. (2008) Detection and characterization of engineered nanoparticles in food and the environment. *Food Addit Contam, Part A Chem Anal Control Expo Risk Assess* 25(7):795–821. DOI: 10.1080/02652030802007553

6. Cornelis G, Hund-Rinke K, Kuhlbusch T, Van den Brink N, Nickel C. (2014) Fate and bioavailability of engineered nanoparticles in soils: A review. *Crit Rev Environ Sci Technol* 44(24):2720–2764. DOI: 10.1080/10643389.2013.829767

7. Montaño MD, Lowry GV, von der Kammer F, Blue J, Ranville JF (2014) Current status and future direction for examining engineered nanoparticles in natural systems. *Environ Chem* 11(4):351–366. DOI: 10.1071/EN14037

8. Taylor DA (2002) Dust in the wind. *Environ Health Perspect* 110(2):A80–A87.

9. Buzea C, Pacheco II, Robbie K. (2007) Nanomaterials and nanoparticles: Sources and toxicity. *Biointerphases* 2(4):MR17–MR71. DOI: 10.1116/1.2815690

10. Cather SM, Dunbar NW, McDowell FW, McIntosh WC, Scholle PA (2009) Climate forcing by iron fertilization from repeated ignimbrite eruptions: The icehouse–silicic large igneous province (SLIP) hypothesis. *Geosphere* 5(3):315–324. DOI: 10.1130/GES00188.1

11. Martin JH, Fitzwater SE (1988) Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature* 331(6154):341–343. DOI:10.1038/331341a0

12. Houghton J (2005) Global warming. *Rep Prog Phys* 68(6):1343–1403. DOI: 10.1088/0034-4885/68/6/R02

13. Maters EC, Delmelle P, Bonneville S (2016) Atmospheric processing of volcanic glass: effects on iron solubility and redox speciation. *Environ Sci Technol* 50(10):5033–5040. DOI: 10.1021/acs.est.5b06281

14. Olgun N, Duggen S, Andronico D, Kutterolf S, Croot PL, Giammanco S, Censi P, Randazzo L (2013) Possible impacts of volcanic ash emissions of Mount Etna on the oligotrophic Mediterranean Sea: Results from the nutrient-release experiments in seawater. *Mar Chem* 152:32–42. DOI: 10.1016/j.marchem.2013.04.004

15. Lin II, Hu C, Li Y-H, Ho T-Y, Fischer TP, Wong GTF, Wu J, Huang C-W, Chu DA, Ko DS, Chen J-P (2011) Fertilization potential of volcanic dust in the low-nutrient low-chlorophyll

western North Pacific subtropical gyre: Satellite evidence and laboratory study. *Glob Biochem Cycles* 25(1):GB1006. DOI: 10.1029/2009GB003758

16. Lindenthal A, Langmann B, Patsch J, Lorkowski I, Hort M (2013) The ocean response to volcanic iron fertilisation after the eruption of Kasatochi volcano: a regional-scale biogeochemical ocean model study. *Biogeosciences* 10(6):3715–3729. DOI: 10.5194/bg-10-3715-2013

17. Bains S, Norris RD, Corfield RM, Faul KL (2000) Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback. *Nature* 407(6801):171–174. DOI: 10.1038/35025035

18. Sigman, DM, Boyle EA (2000) Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* 407(6806):859–869. DOI: 10.1038/35038000

19. Wang Y (2014) Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers. *Chem Geol* 378–379:1–23. DOI: 10.1016/j.chemgeo.2014.04.007

20. Ermolin MS, Fedotov PS (2016) Separation and characterization of environmental nano- and submicron particles. *Rev Anal Chem* 35(4):185–199. DOI: 10.1515/revac-2016-0006

21. Portnyagin M, Hoernle K, Avdeiko G, Hauff F, Werner R, Bindeman I, Uspensky V, Garbe-Schönberg D (2005) Transition from arc to oceanic magmatism at the Kamchatka–Aleutian junction. *Geology* 33(1):25–28. DOI: 10.1130/G20853.1

22. Auer S, Bindeman I, Wallace P, Ponomareva V, Portnyagin M (2008) The origin of hydrous, high-δ^{18}O voluminous volcanism: diverse oxygen isotope values and high magmatic water contents within the volcanic record of Klyuchevskoy volcano, Kamchatka, Russia. *Contrib Mineral Petrol* 157(2):209–230. DOI: 10.1007/s00410-008-0330-0

23. Ermolin MS, Fedotov PS, Ivaneev AI, Karandashev VK, Fedyunina NN, Eskina VV (2017) Isolation and quantitative analysis of road dust nanoparticles. *J Anal Chem* 72(5):520–532. DOI: 10.1134/S1061934817050057

24. Ermolin MS, Fedotov PS, Karandashev VK, Shkinev VM (2017) Methodology for separation and elemental analysis of volcanic ash nanoparticles. *J Anal Chem* 72(5):533–541. DOI: 10.1134/S1061934817050069

25. Karandashev VK, Khvostikov VA, Nosenko SV, Burmii ZP (2018) Stable highly enriched Isotopes in routine analysis of rocks, soils, grounds, and sediments by ICP-MS. Inorg. Mater. 53(14):1432–1441. DOI: 10.1134/S0020168517140084

26. Taylor SR (1964) Abundance of chemical elements in the continental crust; a new table. *Geochim Cosmochim Acta* 28(8):1273–1285. DOI: 10.1016/0016-7037(64)90129-2

27. Menyailov IA, Nikitina LP (1980) Chemistry and metal contents of magmatic gases: the new Tolbachik volcanoes case (Kamchatka). *Bull Volcanol* 43(1):195–205. DOI: 10.1007/BF02597621

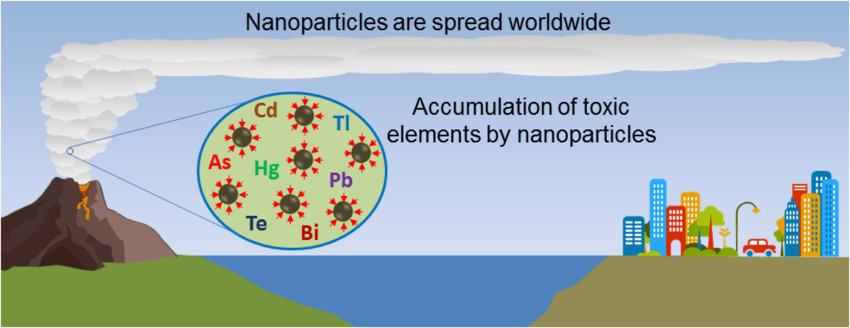
28. Zelenski ME, Fischer TP, de Moor JM, Marty B, Zimmermenn L, Ayalew D, Nekrasov AN, Karandashev VK (2013) Trace elements in the gas emissions from the Erta Ale volcano, Afar, Ethiopia. *Chem Geol* 357:95–116. DOI: 10.1016/j.chemgeo.2013.08.022

29. Zelenski M, Malik N, Taran Yu (2014) Emissions of trace elements during the 2012–2013 effusive eruption of Tolbachik volcano, Kamchatka: enrichment factors, partition coefficients and aerosol contribution. *J Volcanol Geotherm Res* 285:136–149. DOI: 10.1016/j.jvolgeores.2014.08.007

30. Haynes WM (2011) *Handbook of Chemistry and Physics, 92nd Edition,* ed. Haynes WM (CRC Press, Boca Raton), pp 4121–4123.

Highlights

- Nanoparticles (NPs) of volcanic ash were separated and quantitatively analyzed.
- Samples of volcanic ash from different regions of the world were studied.
- NPs are highly enriched by toxic elements as compared to bulk volcanic ash.
- Dramatically high concentrations of Cd, Hg, Tl, Pb, Bi, Se, Te were found in NPs.
- Volcanic ash NPs can serve as an important worldwide carrier for toxic elements.


Nanoparticles are spread worldwide
Accumulation of toxic elements by nanoparticles
Cd
Tl
As
Hg
Pb
Te
Bi