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

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Nanoparticles (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. We demonstrate that NPs of volcanic ash can be an important carrier for toxic metals and metalloids on the global scale. Taking as example volcanoes from different regions of the world (Tolbachik, Klyuchevskoi, Shiveluch – Kamchatka, Far East of Russia, and Puyehue – Puyehue-Cordón Caulle volcanic complex, Andes, Chile) we show that the concentrations of Ni, Zn, Cd, Ag, Sn, Se, Te, Hg, Tl, Pb, Bi in volcanic ash NPs (<100 nm) can be 10-500 times higher than their total contents in bulk samples of ash.

The extreme specific surface and reactivity of NPs cause their high sorption capability. In this sense, volcanic ash NPs are able to pre-concentrate elements from gaseous phase inside the volcano. Taking into consideration the "extreme" conditions of interaction of volcanic ash NP 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 (sublimation) of elements from gaseous phase, while volcanic ash NP may serve as a nucleus for this process.

Uneven distribution of enrichment factor (EF) for different trace elements can be explained by their physical properties, namely, boiling points. 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. High temperature processes during volcanic eruption lead to the vaporization of some elements that assists their pre-concentration by NP. 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. 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.

Hence, NPs of volcanic ash are dramatically enriched by toxic and potentially toxic elements present in volcanic gases and need to be further studied in terms of impact to geochemical processes and possible hazard to human health.