Nature of transition metals on fine and ultrafine particles and the cytotoxicity

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Despite of mounting evidence indicting adverse health effects of ultrafine particle (UFP; <100 nm in diameter), it is difficult to appropriately evaluate the toxicity because of the small size, various shape, mixed chemical state and complicated crystal structure. Transition metals are known to be a factor that causes damage by inducing reactive oxygen species (ROS). The aim of this study is to systematically understand the nature of UFP associated with transition metals and the adverse health effects on lung cells based on the rigorous investigation of crystallo-chemical property of individual UFP in the urban atmosphere and the cytotoxicity assessment.

Inductively coupled plasma mass spectrometry (ICP-MS), X-ray absorption near-edge structure (XANES), scanning and transmission electron microscopy (SEM and TEM) have been employed to rigorously characterize particulate matters collected at urban areas of Fukuoka and Tokyo, and at remote area of Nagasaki. Epithelium cells and macrophage cells were exposed to 0.5-50 ug/ml of SRM 1649a, magnetite nanoparticle, and heavy metal ions, Fe, Mn, Ni and Cr, for 12 hours-26 days in a humidified atmosphere at 37 ºC and 5% CO_2. Cytotoxicity assessment was performed using WST assay. Statistic analysis was carried out based on analysis of variance (ANOVA).

All samples revealed that the dominant Fe speciation of the size fraction >1 μm was Fe-bearing aluminosilicaste, while that in submicron-size fraction was ferric Fe oxides. In the urban UFP, major Fe species was spinel-structured Fe oxides such as magnetite or maghemite, and some of them were mixed with Mn, Cr and Ni. In addition, sulfate and SiO_2 coating were identified in some of those particles.

Both urban UFPs and magnetite nanoparticles did not reveal an acute health effects on the lung cells; however, an exposure to aqueous Mn^{2+} significantly decreased the viability. Ni^{2+} also revealed the cytotoxicity in less extent. These results suggest that the speciation of heavy metals in the solution determine their toxicity, and protein and amino acid may decrease the toxicity of heavy metals by forming complexes. Because Fe-bearing nanoparticles did not decrease the viability, the soluble species of the other toxic metals, namely Mn and Ni, are the primary factor determining the acute cytotoxicity. On the other hand, long life-time of magnetite nanoparticles in alveoli solution resulted in the phase transformation from spherical magnetite to needle-shaped oxyhydroxide, which may result in an increase in the toxicity.

Non-ideal fluid geometry in the mantle and lower crust

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Fluid phases characterize the physical and chemical processes in subduction zones. The conventional view on grain-scale fluid distribution is based on dihedral angle between minerals and fluids in isotropic monomineralic rocks (i.e. ideal "equilibrium" geometry). Natural rocks are, however, composed of anisotropic multiple phases and undergo textural adjustment to minimize interfacial and strain energy such as grain growth and dynamic recrystallization, which results in microstructural complexity. To understand real fluid distribution in deep-seated rocks, we conducted an X-ray CT study of xenoliths from the lower crust and uppermost mantle from Ichinomegata-Maar, NE Japan. All the observed spinel lherzolite, hornblendite, and hornblend gabbro xenoliths contained upto a few vol% of intergranular pores, indicating that the rocks were saturated with a free-fluid phase (Figure 1). The imaged pore fluids are typically polyhedral and tens–hundreds of micrometers in scale; this suggests that they were formed via coalescence of smaller pore fluids. The fluids are localized in interphase boundaries (between different mineral phases), while most of the monomineralic triple junctions lack pore fluids. All these characteristics are consistent with the results of grain-growth experiments in a fluid-bearing bimineralic system[1]; in other words, the role of interfacial energy anisotropy and grain growth are crucial in determining fluid distribution in nature. The geometry, distribution and thus connectivity of fluids cannot be assessed simply from dihedral angles.

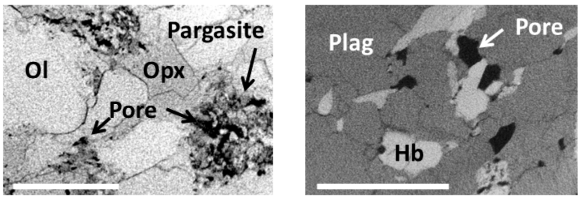

Figure 1: Typical CT images of pores in the lherzolite (left) and hornblende gabbro (right) xenoliths. Scale bars, 500 μm.

[1] Ohuchi and Nakamura (2005) *J. Geophys. Res.* **111**, B01201, doi:10.1029/2004JB003340.

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