

Transformation of Silver Nanoparticles: From the Sewer to the Fly Ash

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Silver-nanoparticles (Ag-NP), used in textiles and cosmetics, will eventually be discharged to the municipal sewer system. We have shown that Ag-NP are efficiently transported along the sewer channel without substantial loss to the biofilm [1]. In the wastewater treatment plant (WWTP), partially sulfidized Ag-NP attach to the wastewater biomass and are removed from the wastewater stream. In parallel, the sulfidation reaction proceeds and the Ag-NP are almost completely sulfidized when leaving the WWTP via the surplus sludge [2]. Ag₂S is very recalcitrant to oxidation as shown in a recent study where digested sludge was stockpiled for several weeks under oxic conditions [3].

In Switzerland sewage sludge is exclusively incinerated, in Germany about 50% with an increasing trend towards thermal sewage sludge disposal and on a EU level, about one third of the sewage sludge is incinerated. In order to allow for later phosphorus (P) recovery, sewage sludge has to be incinerated in monocombustion facilities. Until an economic and ecologic process for P recovery from sewage sludge ashes (SSA) has been found, the majority of the SSA are stored in separate deposits, although in Germany, a small fraction (5%) of the SSA is directly used as fertilizer.

X-ray fluorescence (XRF) analysis of fly ashes collected from monocombustion (fluid bed) facilities revealed Ag concentrations of ~10 mg/kg. X-ray absorption spectroscopy (XAS) analysis showed that Ag in the fly ash was dominantly Ag₂S. This result is in contrast to a recent study concluding that Ag₂S transforms into Ag(0) during the combustion [4], which would possibly have far reaching consequences regarding the direct application of SSA in agriculture. The differences are most likely caused by different combustion conditions between the two studies. We will further investigate the fly ash samples using electron microscopy to assess whether silver is present in the form of nanoparticles.

[1] Kaegi *et al.* (2011), *ES & T*, **49**, 3902 – 3908 [2] Kaegi *et al.* (2013), *Water Research*, doi:10.1016/j.watres.2012.11.060. [3] Lombi *et al.* (2013), *Env.Poll.* **176**, 193–197. [4] Impellitteri *et al.* (2013), *Water Research*, doi:10.1016/j.watres.2012.12.041.

Sulfur and halogen fluxes at mid-ocean ridges: Estimations based on gas compositions in MORB vesicles

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Since S and halogens (F and Cl) form various compounds on the Earth's surface, their geochemical cycles are important issues in the Earth's evolution. Though fluxes of S and halogens at MORs have been estimated using compositions of chilled margins of MORB glasses characterised as those of silicate melts derived from the upper mantle, they may be somewhat overestimated [1]. Plausible estimations based on compositions of volcanic gases released as hydrothermal fluids are necessary. We characterised gas and melt compositions retained respectively in vesicles and solids of MORB glasses and estimated MOR fluxes of S and halogens.

We analyzed MORB glasses collected at 2 sites on East Pacific Rise, 2 sites on Mid-Atlantic Ridge and 2 sites on Central Indian Ridge. After extractions of gases in vesicles by the frozen crushing method [2], concentrations of ³He were measured using a VG-5400 and those of S and halogens were measured using an ICS-2100. Concentrations of S and halogens in solids were measured using a NanoSIMS. We calculated relative molar ratios (S/³He, F/³He and Cl/³He) and estimated MOR fluxes of S and halogens calibrating against the known ³He flux (527 mol/yr [3]).

For vesicle components, global averages of S/³He, F/³He and Cl/³He are (4.2±1.6)×10⁷, (1.4±0.7)×10⁶ and (2.6±1.0)×10⁷. For bulk components, they are (0.3–1.2)×10¹⁰, (1.6–6.5)×10⁹ and (0.7–3.0)×10⁹, respectively. Using these ratios and the known ³He flux, MOR fluxes were estimated to be (2.2×10¹⁰–6.6×10¹²) mol/yr for S, (7.1×10⁸–3.4×10¹²) mol/yr for F and (1.4×10¹⁰–1.6×10¹²) mol/yr for Cl. Assuming the continuous degassing from the solid Earth, formations of atmosphere and ocean can not be achieved by the low MOR fluxes estimated based on vesicle compositions. The amount of S accumulated on the surface are calculated to be 50 times lower than its surface inventory, and halogens are calculated not to be accumulated because of dominant influxes at subduction zones. This implies a possibility that the elements were significantly degassed in the early Earth.

[1] Tajika (1998) *GRL* **25**, 3991-3994. [2] Kagoshima *et al.* (2012) *Geochem. J.* **46**, e21-e26. [3] Bianchi *et al.* (2010) *EPSL* **297**, 379-386.