

Synthesis, reactivity testing and isotopic labelling of ZnO nanoparticles

A.D. DYBOWSKA^{1*}, D. BERHANU¹, S. MISRA^{1,2},
M.N. CROTEAU³, S.N. LUOMA^{1,3}
AND E. VALSAMI-JONES¹

¹Department of Mineralogy, Natural History Museum,
London, UK (*correspondence: a.dybowska@nhm.ac.uk)

²Department of Materials, Imperial College London, UK
³USGS Menlo Park, California, US

Controlled synthesis of monodispersed nanoparticles of well defined size and composition is required to investigate the relationships between particle physicochemical properties and their reactivity/toxicity. Industrially produced nanoparticles are not always pure or monodispersed phases and often suffer from agglomeration. Purpose-made materials on the other hand offer the advantage of controlled material purity, size and agglomeration and thus are much better alternatives for use in toxicity studies [1].

We synthesised model ZnO nanoparticles by forced hydrolysis of Zn acetate in polyol media using a modification of a protocol by Feldmann and Jungk [2]. We obtained 4 sets of particles in the following size ranges: 1) 10-15nm; 2) 150-175nm; 3) 300-320nm and 4) 500-550nm. Size control was obtained by manipulating Zn concentration and changing the Zn precursor. The stability of the colloids was tested in the original media, in DIW, synthetic freshwater and seawater. The solubility of the particles was also evaluated.

The particles were most stable in the original colloidal suspensions (up to 1 month). After centrifuging and resuspending in DIW particle size did not change but after washing in DIW agglomerates formed, probably due to the loss of the protective layer of polymer from particle surfaces. After dilution of the colloids in DIW, particles agglomerated within 24hrs except for the smallest size. Much faster agglomeration was observed in freshwater and seawater. Average particle size, as reported by DLS, increased to 1 micron within an hour of exposure in these media for all sizes tested.

We further synthesised ZnO particles with distinct isotopic composition (enriched with Zn⁶⁷) using isotopically enriched metal powder as a starting material. Preliminary experiments were conducted to characterise waterborne and dietborne uptake of these particles by freshwater snails.

[1] Valsami-Jones *et al.* (2008) *Min Mag* **72**, 515-519.

[2] Feldmann & Jungk (2001) *Angew. Chem. Int Ed.* **40**, 359-362.

In situ iron isotope analysis in Fe-Ti oxides from IODP Hole 1256D (East Pacific Rise)

W. DZIONY*, J. KOEPKE, I. HORN, G. STEINHÖFEL
AND F. HOLTZ

Institut für Mineralogie, Leibniz Universität Hannover;

(*correspondence: w.dziony@mineralogie.uni-hannover.de)

IODP multi-cruise mission 'Superfast Spreading Crust' successfully drilled a complete section of the upper oceanic crust into the underlying gabbros, now representing the first reference profile through fast-spreading upper oceanic crust (Site 1256; eastern equatorial Pacific).

We analyzed iron isotopes in 3 samples from the core representing different lithologies: (1) from the uppermost lava flow (lava pond); (2) from the so-called 'granoblastic dikes' [1]; (3) from the lower gabbro intrusion. We used a UV-femtosecond laser ablation system coupled to a MC-ICP-MS (multiple-collector inductively coupled plasma mass spectrometer). This method allows us to determine iron isotope ratios with a precision of ± 0.1 permil $\delta^{56}\text{Fe}$ ($\delta^{56}\text{Fe} = (56\text{Fe}/54\text{Fe}_{\text{sample}}/56\text{Fe}/54\text{Fe}_{\text{IRMM-14-1}}) \cdot 1000$) and is free of matrix-dependent fractionation effects during ablation [2].

In general, all analyzed minerals show a typical magmatic isotopic signature. Magnetites in the basalts show $\delta^{56}\text{Fe}$ values from -0.2 to 0.2 ‰, and ilmenites from -0.7 to -0.4 ‰. Primary oxides in the gabbro show vast exsolution effects. For a host magnetite we measured a range from 0.3‰ to 0.5‰. The exsolved ilmenite is in the range from -0.2‰ and -0.8‰. We calculated an initial average $\delta^{56}\text{Fe}$ of 0.1‰ for the formerly unexsolved magnetite. We observed a significant difference in the fractionation behaviour of magnetite and ilmenite between the fresh basalt from the lava pond and the thermally overprinted sample from the granoblastic dikes. In the granoblastic dike, for which an equilibrium temperature of $\sim 600^\circ\text{C}$ was estimated by 2-oxide geothermometry [1], the $\Delta^{56}\text{Fe}_{\text{magnetite-ilmenite}}$ values ($\delta^{56}\text{Fe}_{\text{magnetite}} - \delta^{56}\text{Fe}_{\text{ilmenite}}$) are generally high, ranging between 0.5‰ and 0.9‰, while the corresponding values in the lava pond sample (equilibrium temperature of 900°C) are lower, ranging from 0.3‰ to 0.6‰. This is in concordance with the Mössbauer-derived model of temperature-dependent fractionation for this system by Polyakov *et al.* [3],[4].

[1] Koepke *et al.* (2008) *Geochem. Geophys. Geosyst.* **9**, Q07O09. [2] Horn *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 3677-3688. [3] Polyakov & Mineev (2000) *Geochim. Cosmochim. Acta* **64**, 849-865. [4] Polyakov *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, 3833-3846.