

Rationalising nanoparticle sizes measured by AFM, FIFFF and DLS: sample preparation, polydispersity and particle structure

MOHAMMED BAALOUSHA* AND JAMIE LEAD

1 School of Geography, Earth and Environmental Sciences, College of Life and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom, m.a.baalousha@bham.ac.uk (* presenting author)

8e. Towards the fundamentals of nanoparticle interactions with the living world: a life cycle perspective.

This presentation will discuss the sources of variability in the measured nanomaterial (NM) size by different analytical tools including atomic force microscopy (AFM), dynamic light scattering (DLS) and flow-field flow fractionation (FIFFF). The results suggest that differences in NM size measurements between different analytical tools can be rationalised by taking into consideration (i) sample preparation, (ii) sample polydispersity and (iii) structural properties of the NMs.

Appropriate sample preparation is a key to obtain representative particle size distributions (PSDs), and this may vary on a case by case basis. For AFM analysis, an ultracentrifugation method is the optimal method to prepare samples from diluted suspensions of NMs (<1 mg L⁻¹). For FIFFF, the overloading effect, particle-particle and particle-membrane interactions as well as nature of the calibration standards are important determinants of the quality of data. For DLS, the quality of the fitting of the autocorrelation function is a key issue in obtaining correct estimates of particle size. Conversion of intensity PSD to number or volume PSD is promising for determination of number and volume PSD, but hampered by uncertainties in solving and optimizing the autocorrelation function fit.

The differences between the z-average hydrodynamic diameter by DLS and the particle height by AFM can be accounted for by sample polydispersity. The ratio of z-average hydrodynamic diameter: AFM particle height approaches 1.0 for monodisperse samples and increases with sample polydispersity. A polydispersity index of 0.1 is suggested as a suitable limit above which DLS data no longer remains accurate. Conversion of the volume PSD by FIFFF-UV to number PSD helps to rationalise for some of the variability in the measured sizes. The remaining variability in the measured sizes can be attributed to structural variability in the particles and in this case is mainly attributed to the thickness and permeability of the particles/surface coating. For citrate coated NMs, the dFIFFF/dAFM approaches 1 and the particles are described as hard spheres, whereas for PVP coated NMs, the dFIFFF/dAFM deviates toward values greater than one, indicating that these particles are either permeable or non-spherical.

Yttrium mobility during weathering: implications for riverine Y/Ho

MICHAEL G. BABECHUK^{1*}, BALZ S. KAMBER², MIKE WIDDOWSON³

¹Laurentian University, Sudbury, ON, Canada (* presenting author)

²Trinity College Dublin, Dublin, Ireland

³The Open University, Milton Keynes, United Kingdom

Yttrium has similar geochemical properties to the lanthanides and closely mirrors the behaviour of its geochemical twin, Ho, in anhydrous magmatic systems. In the hydrosphere, however, Y is notably less particle reactive than the lanthanides [1] and is more mobile during chemical weathering as a result [e.g., 2]. Here, this behaviour is further explored using chemical transects through two basaltic weathering profiles in India that are preserved in different stages of alteration: the Bidar laterite profile (~50 m) and an incipient to intermediately weathered profile developed across two lava flows (~5 m) near Chhindwara. Both profiles were characterized using major element and high-precision trace element data to establish the progressive compositional changes during chemical weathering.

The parent rock Deccan Traps basalt of both profiles is chemically similar with an average Y/Ho ratio of 25.2 ± 1.1 in the least-weathered samples. In the Chhindwara weathering profile, the enhanced mobility of Y relative to the lanthanides is observed already at the incipient stages of weathering. The preferential loss of Y continues during increasing weathering intensity in the profile as demonstrated by a strong anti-correlation between the chemical index of alteration (CIA; ranging from 35-80) and the Y/Ho ratio (ranging from ~25-23). Yttrium mobility is evident at the scale of the profile as well as across a corestone-saprolite interface (<1 m). The Bidar laterite profile (CIA>90) has highly subchondritic Y/Ho ratios (19.4-14.7) with the exception of one sample in the mottled zone with highly enriched REE abundances and a superchondritic Y/Ho ratio of 30.1.

River waters have superchondritic Y/Ho ratios prior to reaching the estuary (where additional, much more extreme Y/Ho fractionation occurs due to the higher particle reactivity of the HREE), indicating that the greater mobility of Y relative to the HREE during weathering may be sufficient to affect mass balance. Care must be taken to correctly identify the Y/Ho ratio of river water due to the possibility of marine chemical sedimentary rocks in the drainage area and/or contamination from phosphate fertilizers. Using previously published Y/Ho data from eastern Australia rivers [3,4] screened based on P content and salinity to minimize the influence of these complications, a net superchondritic Y/Ho ratio remains. Thus, the weathering behaviour of Y may be more important to the interpretation of riverine Y/Ho ratios than previously considered.

[1] Nozaki et al. (1997) *EPSL* **148**, 329-340.

[2] Hill et al. (2000) *Geology* **28**, 923-926.

[3] Lawrence et al. (2006) *Marine & Freshwater Research* **57**, 725-736.

[4] Lawrence et al. (2006) *Aquatic Geochemistry* **12**, 39-72.