

## Canonical trace element ratios and partitioning during global differentiation

A.W. HOFMANN<sup>1,2\*</sup>

<sup>1</sup>LDEO, Columbia University, Palisades, NY 10964, USA

<sup>2</sup>Max Planck Institute for Chemistry, 55020 Mainz, Germany

(\*correspondence: albrecht.hofmann@mpic.de)

For the past 16 years, the concept of “canonical” trace element ratios - concentration ratios that do not systematically change during global magmatic differentiation processes - has been variously questioned, declared invalid (e.g. [1]), or reaffirmed by many geochemical studies on oceanic basalts. Partitioning of such element pairs is sufficiently similar so that their ratios in melts reflect those of the source. Like isotope ratios, they are useful as tracers of mantle source composition, but they can be more diagnostic of global differentiation processes than the parent-daughter pairs of long-lived radioactive decay systems. Thus, Pb is partitioned similarly to the moderately incompatible LREE during intra-oceanic mantle melting, but it is highly incompatible (similar to U) during arc magmatism leading ultimately to formation of continental crust. Thus, although Pb isotopes do not distinguish well between continental and mantle sources, Pb/Ce ratios are sensitive discriminators. However, the basis for using Pb/Ce as a diagnostic ratio has been criticized, in part because Pb has similar ionic properties as Sr, which is strongly affected by gabbroic plagioclase fractionation, so that primary Pb/Ce ratios should be sufficiently modified to invalidate Pb/Ce as a tracer of mantle composition.

I use recent, comprehensive, high-quality data on the composition of global ocean floor basalts [2, 3, 4] to reassess canonical ratios involving Pb, Nb, Ta, K, U and other trace elements relevant to global differentiation processes. Plagioclase fractionation affects Pb/Ce ratios remarkably little, presumably due to the presence of sulfide during gabbroic fractionation. Overall, the bulk partition coefficient  $D(\text{Pb})$  is between the values for Ce and Pr.  $D(\text{K})$  is between Ta and La, and  $D(\text{Nb})$  between Th and U. The bulk terrestrial K/U ratio is not well defined by MORB data, because K/U varies with absolute trace element enrichment [2].

[1] Sims & DePaolo (1997) *Geochim. Cosmochim. Acta* **61**, 765-784. [2] Arevalo & McDonough (2010) *Chem. Geol.* **217**, 70-85. [3] Jenner & O'Neill (2012) *Geochem. Geophys. Geosyst.* **13**, doi 10.1029/2011gc004009. [4] Gale *et al* (2013) *Geochem. Geophys. Geosyst.* **14**, doi 10.1029/2012GC004334.

## CD-MUSIC to interpret drifting primary charge of ferrihydrite

A. HOFMANN<sup>1</sup>, T. HIEMSTRA<sup>2</sup> AND J. LÜTZENKIRCHEN<sup>3</sup>

<sup>1</sup>Géosystèmes UMR 8217, Université Lille 1, 59655

Villeneuve d'Ascq, France

<sup>2</sup>Dept. Soil Quality, Wageningen University, 6700 AA

Wageningen, The Netherlands

<sup>3</sup>INE, Karlsruher Institut für Technologie, 76344 Eggenstein-Leopoldshafen, Germany

In recent years, « environmental minerals », especially nanoparticles, have come into the focus of research because their short order structure confers them high chemical reactivity. Many of these minerals are formed in heterogeneous soil/water systems under ambient conditions. They reflect transitional, metastable phases that ultimately convert to thermodynamically stable phases, although this process can take very long periods of time. We will focus on surface complexation modeling and show how CD-MUSIC can contribute to understanding dynamic phase transformations.

When 2-line ferrihydrite is synthesized under « environmental conditions », i.e. relatively low ionic strength, no desalination and no drying steps, a material is formed which is marked by drifting of the primary charge over time and blurring of the point of zero salt effect.

Modeling these data with CD-MUSIC suggests that the affinity of electrolyte ions changes during aging of the primary material and that aggregational growth plays a role. We show that the particles' surfaces reflect the subtle changes occurring in the bulk material. Surface complexation modeling helps to decipher them, while classical spectroscopic and X-ray means hardly can.