# Surface complexation and proton promoted dissolution in aqueous apatite systems

ÅSA BENGTSSON, PER PERSSON,ANDREI SHCHUKAREV AND STAFFAN SJÖBERG

Department of Chemistry, Umeå University, S-90187 Umeå, Sweden (Asa.Bengtsson@chem.umu.se; Per.Persson@chem.umu.se; Andrei.Shchukarev@chem.umu.se; Staffan.Sjoberg@chem.umu.se)

Apatites ($Ca_5(PO_4)_3F,Cl,OH$) are the most abundant phosphorus-bearing minerals in nature and they are very important in agriculture as phosphorus containing fertilisers, as well as in medicine as main constituents of mammalian bones and teeth enamel.

The surface chemistry, in terms of surface complexation models, of these minerals is very much unexplored, and the dissolution mechanism is still debated. The objectives with our apatite studies are to characterize possible surface phase transformations and to clarify surface acid/base properties, ion exchange and readsorption reactions involving phosphate and calcium. Furthermore, ligand complexation reactions of these apatites with different organic polycarboxylic acids are also being studied.. Studies are being made in pH ranges with/without extensive dissolution.

The strategy in modelling surface complexation and dissolution of apatite is to yield information provided by different macroscopic techniques: i) potentiometric pH and pF measurements; ii) dissolution characterization with respect to soluble fractions of calcium, phosphate and fluoride; iii) readsorption studies of phosphate, fluoride and calcium, as well as iv) surface charge measurements. Furthermore, this information is combined with surface spectroscopic characterizations using FTIR and XPS methods.

# Crust- mantle dynamics in the early Earth: The $^{142\text{-}143}$Nd and $^{176}$Hf isotopic perspective

V. BENNETT[1], A. BRANDON[2], J. HEISS[1] AND A. NUTMAN[3]

[1]Research School of Earth Sciences, The Australian National University (vickie.bennett@anu.edu.au)
[2]NASA Johnson Space Center, Houston, TX, USA
[3]Chinese Academy of Geological Sciences, Beijing, China

New high precision isotopic data for 3.6 Ga to 3.87 Ga rocks from southwest Greenland and Western Australia show $^{142}$Nd excesses (formed by the decay of now extinct $^{146}$Sm [$t_{1/2}$=103 myr]) of 4 to 20 ppm compared to modern terrestrial compositions and 22-38 ppm with respect to primitive meteorites [e.g. 1]. Combined data from the same samples for the short-lived [$^{146}$Sm-$^{142}$Nd] and long-lived [$^{147}$Sm-$^{143}$Nd] decay schemes directly date the formation of chemically distinct silicate reservoirs during the first 30-50 myr of Earth history, near the time of core segregation. Differences in $^{142}$Nd signatures from coeval rocks from the two most extensive early Archean cratons reveal large-scale chemical dichotomies in the Earth's mantle that persisted for at least the first billion years of Earth history. Temporal variations in $^{142}$Nd signatures track the subsequent incomplete remixing of these very early-formed mantle chemical domains.

Initial Hf isotopic compositions from zircons from the same samples yielding positive $^{142}$Nd anomalies are all within error of chondritic values (using $\lambda^{176}Lu = 1.867 \times 10^{-11} yr^{-1}$). The $^{142\text{-}143}$Nd and initial $^{176}$Hf isotopic compositions of Archean rocks define the time-averaged Lu/Hf and Sm/Nd of their mantle source regions. Generation of positive $^{142}$Nd anomalies as well as $\varepsilon 143_{Nd} \approx +3$ in 3.85 Ga samples, requires an early formed high Sm/Nd reservoir. In contrast, the near chondritic initial $^{176}$Hf/$^{177}$Hf compositions from the same early Archean samples indicate a source with a long-term chondritic Lu/Hf ratio. Thus the trace element pattern of the pre-3.85 Ga depleted mantle differs from the MORB source mantle, which is characterized by both supra-chondritic Lu/Hf and Sm/Nd. Significantly this suggests that typical continental crust with low Lu/Hf and Sm/Nd ratios is not the primary complimentary enriched reservoir to the early depleted mantle. Rather these observations support models for very early (30-60 myr after $T_0$) silicate differentiation of the Earth [e.g. 2] unrelated to early continental crust formation. Although >4.0 Ga zircons, including those from the Jack Hills, Western Australia, provide evidence that some Hadean continental crust was present, it may have been of only limited extent.

## References

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