Competitive adsorption between phosphate and carboxylic acids: Quantitative effects and molecular mechanisms

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A series of carboxylic acids with increasing number of functional groups were evaluated for their competitive ability towards phosphate at the water-goethite interface.

A multi-technique experimental approach was used and both quantitative adsorption data and molecular spectroscopic information was collected. The work was carried out in series of batch experiments with varying ligand combinations (phosphate and/or one of the organic acids) and with pH ranging from 3-9. *in situ* ATR-FTIR spectroscopy was extensively used to evaluate the speciation and adsorption mechanisms of phosphate and the carboxylic acids. In addition, ionic chromatography, UV, and atomic absorption spectrometry were used to gain numerical adsorption and dissolution data.

The efficiency of the organic acids was found to be in the order: oxalate < citrate < 1,2,3,4-butanetetracarboxylic acid ≈ Suwanee River Standard Fulvic Acid 1S101F < mellitate (a benzenehexa-carboxylate). This indicates that an increasing number of carboxylic groups enhances the capacity to compete with phosphate. Infrared spectroscopy conclusively show that the underlying reaction is not a ligand-exchange reaction between inner sphere surface complexes, but rather a competition between partially protonated phosphate and hydrogen bonded outer sphere carboxylate species. There are also indications that the mechanisms behind competition are pH dependent, and that the carboxylates act as proton donors at low pH and as proton acceptors at higher pH.

A critical look at the Late Heavy Bombardment hypothesis

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The Early Heavy Bombardment and the hypothesized Late Heavy Bombardment (LHB) may have played an important role in the impact frustration of the earliest life on Earth. We review the arguments for and against a Late Heavy Bombardment (LHB) of the Moon in the interval from ~3.8 to 4.0 Gya and present a new analysis of the largest and earliest lunar impacts (Lineweaver & Norman 2009). Our preliminary analysis of the ages (given current uncertainties) and cumulative impact diameter of lunar basins does not support the LHB. Our analysis does not indicate a pronounced spike in the bombardment rate at 3.85 +/- 0.1 Ga. Corrections to our analysis to compensate for saturation effects in the oldest craters, the inclusion of an estimated ~14 pre-Al Khwarizmi/King obliterated basins to the analysis and an iterative approach to determining the impact rate, all support the idea that the highest impact rate pre-dates the LHB date of 3.85 +/- 0.1 Ga. The decrease in the number of lunar meteorites with ages older than ~4 Ga is probably best explained as a selection effect of lunar meteorites (and glass spherules) sampling the current surface of the Moon, not the largely buried, older than 4 Ga surface. The evidence for a pre-South-Pole-Aitken or pre-4 Ga heavy bombardment has propbably been buried by its own, and subsequent impact blankets.

Our analysis does not support the LHB hypothesis as articulated by Ryder (2002, 2003), nor do we find the data from impact breccias, glass spherules or lunar meteorites supportive of the LHB. We highlight the importance of dating South Pole Aitken and the other earliest impact basins to convert a relative basin chronology into an absolute chronology of the impact history of the Moon and Earth.

[1] Lineweaver & Norman (2009) 'The Bombardment History of the Moon and the Origin of Life on Earth' Australian Space Science Conference Series: Proceedings of the 8th Australian Space Science Conference, eds W. Short & I. Cairns, National Space Society of Australia, in press. [2] Ryder (2002) *J. Geophys. Res.* **107**, E4 5022, 10.1029. [3] Ryder (2003) *Astobiology* **3** (1), 3-6.