

## Effects of adsorption processes on the interactions of phthalic acid and goethite

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It is known that the oxidation of organic matter and dissolution of minerals are promoted by interactions of organic matter and minerals. It is very important to examine the adsorption process of organic matter on the mineral surface for understanding these interactions. The adsorption behaviour of humic acids to goethite is one of the representative organic-mineral interactions on the earth surface.

The humic acid is a complex macromolecule containing reactive functional groups such as carboxyl (COOH). Phthalic acid, containing an aromatic ring with 2 carboxyl groups, was employed here as a model compound simulating the humic acid. The adsorption behavior of phthalic acid to goethite was studied by adsorption experiments and attenuated total reflection infrared (ATR-IR) spectroscopy. Results of adsorption experiments in pH 3-10 of phthalic acid on goethite were analyzed by surface complexation modeling (Extended Triple Layer Model: ETLM). These analyses indicated that the adsorbed states of phthalic acid on goethite are expected to be mainly in the inner-sphere complex in low pH solutions, while the outer-sphere complex is predominant in neutral pH.

Adsorption kinetics of phthalic acid on goethite was studied by continuous measurements of ATR-IR. The results are compared with dissolution rates of goethite obtained by batch experiments. Effects of adsorption of phthalic acid on goethite surface on the goethite dissolution rates are discussed.

## Identifying a lunar impact at ~3.3 Ga using $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometry

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Much of the absolute chronology of impacts on the lunar surface has been quantified with  $^{40}\text{Ar}/^{39}\text{Ar}$  "plateau ages" of melt fragments [1]. The primary assumption is that the melt fragments collected from ejecta were generated by impacts. An alternative approach is to quantify partial resetting ages of minerals, as observed in initial steps of  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra. Thermochronometry may constrain the conditions of partial diffusive Ar loss *subsequent* to the initial Ar closure age. High-resolution  $^{40}\text{Ar}/^{39}\text{Ar}$  thermochronometry conducted on 9 regolith particles from Apollo 16 soil 63503 clearly reveals a short-duration heating event at  $3.3 \pm 0.1$  Ga, which partially reset both ~3.9 and ~4.2 Ga aged rocks. For each sample, the observed Ar diffusion kinetics constrains a non-unique family of time-temperature pairs which would perturb the  $^{40}\text{Ar}$  distribution at 3.3 Ga to yield the observed  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum. Assuming all 9 samples experienced a common thermal event at 3.3 Ga, we constrain the unique solution by minimizing the differences between them. An instantaneous increase from ambient lunar near-surface conditions to ~510°C for ~2.5 hours at 3.3 Ga would best explain the entire dataset, although ~days spent cooling to lower temperatures are permissible. The best-fit solution may represent the mean thermal state of the rocks during an impact event at ~3.3 Ga. It is not yet clear whether this was a local small impact event or whether this is a signature of a distant larger impactor. A variety of independent observations also reveal a possible event at ~3.3 Ga, including  $^{40}\text{Ar}/^{39}\text{Ar}$  partial resetting ages of other Apollo 16 and 17 samples [2,3], and  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages observed in a significant number of lunar meteorites [4] and lunar impact spherules from Apollo 14 and 12 [5,6]. We will discuss the possibility and implications of one or more lunar impacts at ~3.3 Ga.

[1] Stoffler *et al.* (2005) *RiMG* **60**, 519-596 [2] Bernatowicz *et al.* (1986) *LPSC* **16**, A42-43 [3] Darymple & Ryder (1996) *JGR* **101**, 26069-20084 [4] Cohen *et al.* (2005) *MPS* **40**, 755-777 [5] Culler *et al.* (2000) *Science* **287**, 1785-1788 [6] Levine *et al.* (2005) *GRL* **32** L15201