Dissolved organic matter concentration and character influence Hg-S bioavailability to Hg-methylating bacteria

ANDREW M. GRAHAM[1*], ALLYSON L. BULLOCK[1], GEORGE R. AIKEN[2], AND CYNTHIA C. GILMOUR[1]

[1]Smithsonian Environmental Research Center, Edgewater MD, USA, grahaman@si.edu (*presenting author)
[2]U.S. Geological Survey, Boulder, CO, USA

Mercury methylation occurs primarily in mildly sulfidic environments where nanoparticulate forms of Hg-S are increasingly recognized to be of significance [1,2]. In this study, we sought to elucidate the role of dissolved organic matter (DOM) in altering the bioavailability of Hg-S to a model Hg-methylating bacterium, *Desulfovibrio desulfuricans* ND132. Methylmercury (MeHg) production by strain ND132 was evaluated in short-term washed cell assays in Hg-S-DOM solutions containing DOM isolates of varied origin, size, and composition, as well as a wide range of [Hg]/[DOM] and [Hg]/[sulfide] concentration ratios.

Under mildly sulfidic conditions (1-10 μM total dissolved sulfide), MeHg production was found to increase linearly with increasing DOM concentration, while relative bioavailability (i.e., fractional Hg methylation) increased logarithmically with increasing [DOM]/[Hg] ratio. Equilibrium speciation calculations indicated that Hg binding to DOM-thiols did not outcompete Hg binding to sulfide, and that solutions were supersaturated with respect to β-HgS(s) (metacinnabar) under most experimental conditions. We hypothesize that DOM enhanced MeHg production by stabilizing small, poorly crystalline HgS particles against growth/aggregation. Supporting this hypothesis, we found no DOM-dependent enhancement in Hg methylation in the presence of a strong Hg-binding ligand (L-cysteine) at concentrations sufficient to outcompete sulfide for inorganic Hg. Further, we found that while all DOM isolates tested ($n = 12$) enhanced MeHg production to some degree (2- to 25-fold enhancement at 20 mg C/L and 0.5 nM added Hg), the enhancement in Hg methylation correlated with the DOM isolates' specific UV absorbance (SUVA), a measure of DOM size and aromaticity. This finding is significant in that DOM size and aromaticity have been demonstrated to be key characteristics controlling HgS precipitation and dissolution [3], suggesting a link between dynamics of HgS precipitation/dissolution, Hg uptake, and Hg methylation.

Overall, our results point to the limits of existing equilibrium-speciation based models for Hg uptake and methylation. In addition to Hg and sulfide concentrations, DOM concentration and character are potentially important variables for predicting *in-situ* Hg-methylation rates in natural systems.

[1] Deonarine *et al.* (2008) *Environ. Sci. Technol.* **43**, 2368-2373. [2] Gerbig *et al.* (2011) *Environ. Sci. Technol.* **45**, 9180-9187. [3] Waples *et al. Geochim. Cosmochim. Acta*. **69**, 1575-1588.

Apollo 15 zircons reveal age of young impact

MARION L. GRANGE[1*], ALEXANDER A. NEMCHIN[1], ROBERT T. PIDGEON[1] AND CHARLES MEYER[2]

[1]Curtin University, Perth, Australia, m.grange@curtin.edu.au
[2]Johnson Space Center, Houston, USA.
(* presenting author)

We have investigated microstructures of zircon and apatite grains, their textural context and U-Pb ages, in Apollo 15 sample 15405, aiming to extend the existing database consisting of Apollo 14 and 17 breccia samples. Sample 15405 was chipped from a boulder at Station 6A, south of the landing site and close to the Apennine Front. It is a clast-bearing impact melt breccia, with a crystalline matrix, similar in chemistry to KREEP basalt, and containing KREEP basalt and quart-monzodiorite (QMD) clasts. It contains zircon and apatite grains both within the matrix and in QMD clasts.

Zircon grains in the matrix are abraded or broken fragments. Zircons in both matrix and clasts are anhedral, showing oscillatory and sector zoning in CL. Previous work [1] on zircon included in QMD clasts indicated a disturbed U-Pb system in the grains with an upper concordia intercept at 4294±26 Ma and a lower intercept at 1320 +240/-280 Ma (2σ). New data show comparable patterns, with no age distinction between zircon from the matrix and from clasts: both types show concordant and discordant ages, although oscillatory zoned zircon are systematically concordant. The combination of concordant analyses gives the age of 4335±7 Ma (2σ). When combining these data with discordant ages from zircon and apatite, a lower intercept is obtained at 1570±51 Ma (2σ). In addition, a single spot in one zircon shows a concordant age at 2053±14 Ma (1σ).

These young U-Pb ages have never been found before in lunar zircons that are usually >3.9 Ga. It indicates that the relatively robust U-Pb system in zircon has been severely disturbed at ~1570 Ma (and maybe also at ~2.05 Ga). Such late disturbance is also recorded in Ar-Ar ages at ~1.3 Ga [2] and ~2.1 Ga [3]. These authors [3] interpreted these young ages as disturbance following close-by impacts that they tentatively identified as Aristillus and Autolycus, respectively.

If these young U-Pb ages of zircon can be associated with a particular impact event, this would be the first time a clear link can be established between a specific impact event and a zircon age. This would have major implications for constraining variations in the flux of impactors through the history of the inner Solar System, as so far only relative ages of craters exist. Previous studies [3] showed that even poorly defined ages of specific crater, i.e. much less precise that what can be obtained using zircon, can dramatically increase our understanding of the impact flux of the Moon, and by extension of the Earth. Such opportunities have to be fully explored making breccia 15405 one of the key samples in the lunar collection.

[1] Meyer et al. (1996) *MAPS* **31**, 370-387. [2] Bernatowitz et al. (1978) *Proc. LPSC* **9th**, 905-919. [3] Ryder et al. (1991) *Geology* **19**, 143-146.