

## When the surface is not what you think it is

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More than a century ago, chemists began to explore the thermodynamic and kinetic relationships between solids and fluids in nature. Goldschmidt attempted to classify them and Garrels, Christ, Krauskopf, Stumm, Schindler, Helgeson, Sposito and many others taught us to use thermodynamic relationships to predict natural system behaviour. When it has failed, we have often blamed kinetics.

About two decades ago, surface sensitive techniques first demonstrated that a calcite surface is not simply a termination of the bulk atomic structure. Surface atoms shift position, water delocalises charge on dangling bonds, adventitious carbon is ubiquitous and even on surfaces that appear dry, an adsorbed water film promotes recrystallisation[1]. New instruments allow us to see ever closer, giving new insights into the properties and behaviour of nano-particles and mineral-fluid interfaces so there is now little doubt. Surfaces are not simply where the bulk terminates.

Still, however, there are many cases where natural surfaces do not behave as we assume they ought to[2]. Molecular modelling, atomic force microscopy (AFM) and X-ray reflectivity show that water, structured at calcite surfaces, is displaced by ethanol and the alcohol orders itself, almost like a lipid layer. Adhesion properties change in response to ionic strength but reproducibility is elusive on ideal surfaces, whereas mineral grains plucked from sandstone, with their natural adventitious carbon, behave consistently. It is this organic "contamination" on these mineral surfaces that determines their hydrophilic properties, not the mineral beneath. Recent AFM studies have also revealed that sediment grain surfaces are frequently covered by nanocrystals of clay. These are far too thin for detection by X-ray diffraction so they have previously gone unnoticed but in some cases they cover significant portions mineral surfaces, meaning they can control water-rock properties. Finally, sea creatures produce aragonite and calcite in crystal forms tailored to their needs but these biogenic materials behave differently than inorganically produced minerals, even when organic components that remain associated with the biominerals are present only in the parts per billion range.

Materials adsorbed on mineral surfaces change properties in unexpected ways. By understanding surfaces better, we are likely to discover why large scale geological systems do not always behave as thermodynamics leads us to expect. We can hope that our new insight brings us to a point where we might have less need of the excuse "kinetically hindered".

[1] Stipp and Hochella (1991) *GCA* **55**, 1723-1736; Stipp et al. (1994) *Amer. Min.* **81**, 1-8; Stipp (1999) *GCA* **63**, 3121-3131. [2] Bohr et al. (2010) *GCA* **74**, 5985-5999; Cooke et al. (2010) *Langmuir* **26**, 14520-14529; Sand et al. (2010) *Langmuir* **26**, 15239-15247; ; Hassenkam et al. (2011) *PNAS*, 7307-7312; Hassenkam et al. (2011) *Coll. Surf. A* **390**, 179-188; Skovbjerg et al. (2012) *GCA in review*; Pasarin I.S. et al. (2012) *Langmuir in press*.

## Mechanisms controlling <sup>238</sup>U/<sup>235</sup>U isotopic fractionation in low- and high-temperature environments

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Recent studies have documented sizeable, permil-level isotopic fractionation between <sup>238</sup>U and <sup>235</sup>U in low-temperature environments, facilitated by analytical advancements in multiple-collector ICP-MS (MC-ICPMS) [1,2]. Variability in <sup>238</sup>U/<sup>235</sup>U has a direct impact on the accuracy of the U decay series chronometers, requiring the <sup>238</sup>U/<sup>235</sup>U of every sample to be characterized, and the revision of important cosmo- and geo-chronological models. Further efforts have focussed on investigating the processes controlling <sup>238</sup>U/<sup>235</sup>U isotope fractionation, especially during U reduction. To this end, the <sup>238</sup>U-<sup>235</sup>U isotope system offers significant potential as a monitor of redox conditions in U bioremediation studies [3], and as a paleo-redox tracer of the extent of anoxia in the historic oceans [4] to complement the growing inventory of other redox-sensitive metal isotope tracers (e.g. Mo and Fe) which each have differing redox potentials and respond to anoxia at different rates. However, additional studies are required to gain an improved understanding of the mechanisms controlling <sup>238</sup>U-<sup>235</sup>U isotope fractionation before these applications can be fully explored, as the available datasets show some contrasting U isotopic behaviour during U reduction.

Using MC-ICPMS, we report <sup>238</sup>U/<sup>235</sup>U observations for samples collected from a range of low- and high-temperature environments. A <sup>233</sup>U-<sup>236</sup>U double spike was employed to monitor instrumental mass fractionation, allowing variations in <sup>238</sup>U/<sup>235</sup>U to be resolved at the 0.005 % level (2σ) on 50 ng U sample sizes, and at the 0.003 % level (2σ) on larger sample sizes by pooling the data of replicate analyses. In all of the low-temperature environments we have investigated, the magnitude and direction of the <sup>238</sup>U/<sup>235</sup>U isotopic fractionation is consistent with the 'nuclear field shift effect' [5] as the dominant fractionation mechanism, favouring enriched <sup>238</sup>U/<sup>235</sup>U compositions in the reduced reaction product where the electron density near the nucleus is lower. Our results for a wide range of meteorites [6,7] and volcanic terrestrial samples reveal small (0.01 % level) but resolvable variations in <sup>238</sup>U/<sup>235</sup>U in high-temperature environments. Further efforts should focus on identifying U fractionation mechanisms in high-temperature systems by linking <sup>238</sup>U/<sup>235</sup>U to U concentration and oxidation state. Bulk samples and mineral aggregate sub-samples spanning the primitive to differentiated meteorite classes should also be investigated to determine the extent to which <sup>238</sup>U/<sup>235</sup>U variations are controlled by U isotope heterogeneity or extant <sup>247</sup>Cm effects in the early solar system versus U 'stable' isotope fractionation during subsequent chemical and thermal processing.

[1] Stirling et al. (2007). *EPSL* **264**, 208-25; [2] Weyer et al. (2008). *GCA* **72**, 345-59; [3] Bopp et al. (2010). *Env. Sci. Tech.* **44**, 5927-33; [4] Montoya-Pino (2010). *Geol.* **38**, 315-18; [5] Bigeleisen (1996). *J. Am. Chem. Soc.* **118**, 3676-80; [6] Amelin et al. (2010). *EPSL*. **300**, 343-350; [7] Kaltenbach et al. (2012). *LPSC* #1691.