

## <sup>17</sup>O anomalies in sedimentary silica and oxides

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Recent oxygen isotope measurements demonstrate small but significant deviations from a single mass dependent fractionation line among terrestrial materials [1, 2]. These anomalies confirm theoretical expectations of variation in the  $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$  relationship for equilibrium and kinetic isotope fractionations such that kinetic processes result in a relatively shallow slope (0.513) and equilibrium processes result in a steeper slope (0.529) [3]. Here we present  $\Delta^{17}\text{O}$  data for sedimentary silica and oxides, including cherts and banded iron formation (BIF) materials. We report  $\Delta^{17}\text{O}$  relative to a reference line ( $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ ), slope  $0.530 \pm 0.003$  (95% conf, MSWD = 1.07 [4]), that we produced from analysis of igneous and high-grade meta-igneous garnet, albite, pyroxene, olivine and quartz. This slope is higher than slopes previously generated for garnets ( $0.527 \pm 0.001$ ) and quartz ( $0.524 \pm 0.001$ ) in other laboratories [2], but within error of the slope predicted for equilibrium fractionation (0.529).

Archean cherts yield average  $\delta^{18}\text{O}$  values of  $21.6 \pm 0.3\%$  (SMOW) and  $\Delta^{17}\text{O}$  values of  $-0.13 \pm 0.01\%$ .  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of Phanerozoic cherts average  $31.8 \pm 2.0\%$  and  $-0.16 \pm 0.01\%$ , respectively. BIFs from Greenland yield  $\delta^{18}\text{O}$  of  $10.8 \pm 1.7\%$  and  $\Delta^{17}\text{O}$  of  $-0.04 \pm <0.01\%$ . Slopes needed to produce these results by fractionation with respect to seawater (assuming  $\delta^{18}\text{O}$  is 0‰ SMOW) average 0.523, 0.524 and 0.526 (std. err.  $<0.001$ ) for Archean cherts, Phanerozoic cherts and BIFs, respectively. If initial water  $\delta^{18}\text{O}$  is varied by  $\pm 5\%$  the calculated slopes all remain less than 0.527.

These  $\Delta^{17}\text{O}$  results demonstrate detectable  $^{17}\text{O}$  anomalies in sedimentary silica and oxides. Negative  $\Delta^{17}\text{O}$  values in Phanerozoic cherts indicate that such anomalies can be produced in marine authigenic minerals within an oxygenated atmosphere; i.e. they are not likely connected to photochemical  $^{17}\text{O}$  anomalies. We hypothesize that these compositions result from mass dependent, kinetic fractionations associated with silica precipitation from seawater.

[1] Barkan & Luz (2005) *Rap. Comm. Mass. Spectr.* **19** 3737–3742. [2] Rumble *et al.* (2007) *GCA* **71**, 3592–3600. [3] Young *et al.* (2002) *GCA* **66**, 1095–1104. [4] Ludwig (2003) [http://www.bgc.org/isoplot\\_etc/software.html](http://www.bgc.org/isoplot_etc/software.html).

## Water intermittent dynamics over a colloidal interface: Probing adsorption and relocation statistics in confinement

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Water confined in the vicinity of mineral surfaces is a ubiquitous situation encountered in geological, physical, biological, and industrial systems. As a result, much research effort has been devoted to understand the effect of confinement and surface forces on water dynamics. A coarse grain picture of this dynamics over a surface can be considered as an intermittence of adsorption steps and bulk relocations from one point to another point of the interface. Adsorption statistics such as the adsorption time distribution and its first moment reflect the degree of interaction of the molecule with the colloidal interface. The relocation statistics strongly depends on the shape of the colloidal particle, the surface forces and the bulk confinement [1-3]. In this talk, a theoretical analysis of the intermittent dynamics (ID) is first proposed for different interfacial geometries [2-3]. Direct comparisons with recent Molecular Dynamics simulations are discussed [4]. In the second part, we present an experimental investigation of the ID, using NMR relaxometry for various colloidal systems (flat colloidal clay particles [4], imogolite strands [5], plaster pastes [6]). Comparison with analytical derivations is discussed. Evaluation of the fluid-surface interaction in term of 'nano-wettability' is emphasized.

[1] Levitz (2005) *J. Phys. Condens. Matt.* **17**, S4059. [2] Levitz, Grebenkov, Zinsmeister, Kolwankar & Sapoval (2006) *Phys. Rev. Lett.* **96**, 180601. [3] Levitz, Zinsmeister, Davidson, Constantin & Poncelet (2008) *Phys. Rev. E* **78**, 030102 (R). [4] Bonnaud, Coasne & Pellenq (2010) *J. Phys.Chem.*, in press. [5] Levitz & Korb (2005) *Europhysics Letters* **70**, 684. [6] Korb & Levitz (2008) *Proceedings of MRPM* **9**.