

The effect of surface chemistry on dissolution rates of CaF₂ suggests a new dissolution mechanism

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We investigated how during dissolution differences in surface chemistry affect the evolution of topography of CaF₂ pellets with a microstructure similar to UO₂ spent nuclear fuel [1]. 3D confocal profilometry and atomic force microscopy were used to quantify retreat rates and analyze topography changes on surfaces with different orientations as dissolution proceeds up to 468 hours. A NaClO₄ (0.05 M) solution with pH 3.6 which was far from equilibrium relative to CaF₂ was used.

Measured dissolution rates depend directly on the orientation of the dissolving surfaces. The {111} is the most stable plane with a dissolution rate of $(1.2 \pm 0.8) \times 10^{-9} \text{ mol.m}^{-2}.\text{s}^{-1}$, and {112} the least stable plane with a dissolution rate 33 times faster than {111}. Dissolution rates were found to be correlated to surface orientation which is characterized by a specific surface chemistry and therefore related to surface energy. It was proposed that every surface is characterized by the relative proportions of the three reference planes {111}, {100} and {110}, and by the high energy sites at their interceptions.

Based on the different dissolution rates observed and ab initio simulations we propose a dissolution model to explain changes of topography during dissolution [2]. Surfaces with slower dissolution rate, and inferred lower surface energy, tend to form leading to an increase of roughness and surface area. This adjustment of the surface during dissolution suggests that dissolution rates during early stages of dissolution are different from the later stages. The time-dependency of this dynamic system needs to be taken into consideration in geosciences and the nuclear waste disposal management when predicting long-term dissolution rates.

[1] Godinho et.al. (2011) *J. Nucl. Mat.* **419**, 46-51.

[2] Godinho et. al. (2012) *Geochim. Cosmochim. Acta* (in review)

Application of Light Isotopes as a Tool for Watermasses tracing – Results of South Atlantic JC-057 Cruise

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Introduction

As part of the JC-057 cruise, filtered seawater samples were collected from 18 stations at 24 different depth. The samples were directly measured using a L-1102i PICARRO water analyzer (cavity ring down spectrometer, CRDS). Each sample result represents the mean value of four different injections, and for a batch of each six samples a standard and a test sample were measured. Typical combined uncertainty is 0.7‰ for $\delta(D)$ and 0.2‰ for $\delta(^{18}O)$.

The obtained results shown that light isotopes values are valuable tools to identify watermasses. An example of the obtained output is shown in Fig 1, where is possible, for example, to identify different water masses as, for example, South Atlantic Central Water (SCAW) at the surface and the North Atlantic Depth Water (NADW), at intermediary depth, starting at a latitude of about 40°S. Interesting also to note is the inflow of a bottom water mass at 45° S. Good correlation to salinity [1] (Fig. 2) and nutrients, as fosfate, was observed, in particular, of $\delta(D)$ values.

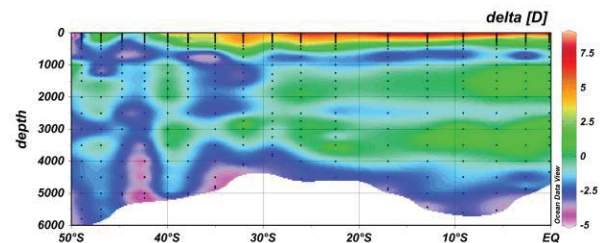


Figure 1: Isopleth of $\delta(D)$ values

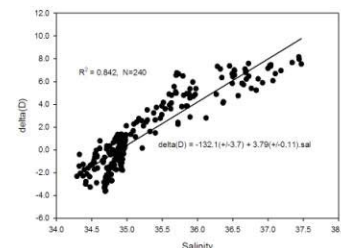


Figure 2: $\delta(D)$ and salinity relationship

Conclusions

On a very simple way, applying CRDS, it was possible to trace the different water masses acting at the South Atlantic along the South American coast.

Povinec, (2011) *Earth and Planetary Letters* **302**, 14-26