How to measure the pure dissolution kinetics of a soft mineral?

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Among interfacial processes, dissolution of minerals is present in countless problems: durability of mineral materials, management of nuclear wastes, sequestration of atmospheric CO2, pollution of drinking water … The modelling of all these situations requires the knowledge of the mineral dissolution kinetics, which in turn necessitates, to be reliable, a precise understanding of all the basic mechanisms intervening in the reaction.

The understanding of these fundamental mechanisms has progressed during the last decade. For instance, the use of molecular simulations and atomic-scale microscopy has enabled to understand the weak role of etch pit density on the dissolution kinetics, or the role of the surface history on this kinetics. But beside these successes, the measurement of the pure dissolution kinetics, and accordingly the identification of the basic processes driving the kinetics, is often a delicate experimental task.

We present here two situations of apparently inconsistent dissolution kinetics results of a soft mineral in the literature. In the two cases, a detailed data analysis and the identification of external phenomena blurring the results have permitted to gain the pure dissolution kinetics and then determine the basic processes:

- The dissolution rate constants of gypsum in water measured by various bulk methods are inconsistent. We have shown that the removal of the contribution of mass transport to these dissolution rates enables to obtain the pure chemical reaction rate constant of gypsum in water, coherent with all the measurements.

- The dissolution of gypsum proceeds via the migration of atomic steps. The step velocities, measured by Atomic Force Microscopy, show a large dispersion. We have shown that this dispersion stems from the influence of the AFM tip. The force applied by the lever increases locally the solid elastic energy, which promotes dissolution, and hence the step velocity.

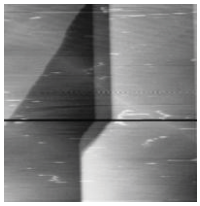

Figure 1: AFM picture of the cleavage plane of gypsum during dissolution. The black line shows the AFM tip path during a step velocity measurement performed just before the picture.

Microbial production of methylmercury from Hg(0)

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Introduction

Mercury [Hg] is a global pollutant and its accumulation in food as methylmercury [MeHg] has caused serious public health crises this past century. In order to predict the fate and deleterious effects of Hg in the environment, a mechanistic understanding of MeHg production in aquatic ecosystems is required. Previous studies have elucidated the mercuric [Hg(II)] species that are bioavailable to methylating microbes [1,2]. Although it is generally assumed that elemental Hg [Hg(0)] is unavailable for biologic methylation [3], the uptake and transformation of Hg(0) by anaerobic Hg-methylating bacteria have never been tested. Here we demonstrate that *Desulfovibrio desulfuricans* ND132 produces MeHg when provided with dissolved Hg(0) as its sole mercury source.

Materials and Methods

D. desulfuricans ND132 was grown to exponential phase and subsequently exposed to a constant source of dissolved Hg(0) under anaerobic conditions in the dark. At periodic intervals, samples were collected for total non-purgeable Hg analysis. These samples were purged with N_2 gas, digested with BrCl, and analyzed for Hg by cold vapor atomic absorption spectroscopy. Cell suspensions containing non-purgeable Hg were filtered (0.2 μm filter) to determine the amounts of dissolved and cell-associated Hg. To examine the chemical speciation of cell-associated Hg, cells were collected and examined using X-ray absorption near edge structure (XANES) spectroscopy. Finally, ND132 cultures were analyzed for MeHg production by distillation, ethylation-gas chromatography, and cold vapor atomic fluorescence spectroscopy.

Results and Discussion

We observed a rapid transformation of Hg(0), with bacterial cultures producing ~40 μg/L of non-purgeable Hg within 30 min. Examination of the Hg L_{III}-edge position in the XANES spectra revealed that Hg oxidation to Hg(II) had occurred. After 24 h of incubation, *D. desulfuricans* ND132 produced up to 700 μg/L of non-purgeable Hg and 50 μg/L of MeHg. Similarity between the XANES spectra of bacterial samples at 30 min. and 24 h and a Hg-$(cysteine)_3$ reference compound suggested that most of the Hg(II) was associated with cells via coordination with thiol functional groups. The formation of Hg-thiol structures is consistent with Hg(II) uptake into the cell, since Hg(II) transfter into and within bacterial cells is governed by thiol-containing protiens [3]. The results of this study demonstrate a previously unrecognized source of MeHg in the environment.

[1] Benoit *et al.* (1999) *Appl. Environ. Microbiol.* 67, 51-58. [2] Schaefer & Morel (2009) *Nature Geosci.* 2, 123-126 [3] Fitzgerald *et al.* (1991) *Water, Air, Soil Poll.* 56, 745-67. [4] Barkay *et al.* (2003) FEMS *Microbiol. Rev.* 27, 355-84.