

FINAL REPORT PROGRAM LEFE

Program LEFE/ CYBER/EC2CO	Project Title KINETICS	Years 2015-2017
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<p>Context KINETICS addresses scientific questions related to processes occurring at the land-ocean interface. Knowing that the riverine particulate element flux is up to two orders of magnitude larger than the dissolved one, the idea is to quantify the amount of chemical species released by dissolution or desorption once these particles are entering in seawater.</p> <p>Objectives / scientific questions KINETICS focused on the measurement of the fate of two nutrients and their isotopes (Si and Ni) under agitated conditions as what is observed under sudden floods or under the pressure of the waves on the beach at the surf zone. Experimental devices allowed simulating these turbulent conditions and following the kinetics of release of these elements.</p> <p>Main results A first set of experiment was conducted with a sand of Fontainebleau, i.e. made of homogeneous grains of pure quartz that were put in contact with seawater and freshwater, under static mode, moderate and strong agitations, at room temperature and under abiotic conditions. We demonstrate that i) the kinetic of quartz dissolution (and DSi release) is very slow when static and considerably increases with an agitation of 230 rpm (Figure 1); ii) we observe similar kinetic accelerations in seawater and in freshwater (not shown); iii) we tested the influence of the water/rock ratio: not surprisingly, the release of dissolved Si (DSi) is more pronounced when W/R are low (Figure 2b). A modeling allowed simulating these dissolution rates: we adapted a “shrinking sphere model” developed in metallurgical domain. A good fit with the data is obtained in quasi-stationary mode considering that the particle dissolves faster in an agitated media <u>because the boundary layer where the transport of aqueous species is driven by diffusion</u>—slower than advection- is very thin. This allowed us to use the Nienow correlation. This relationship is valid when particles are dissolving in an agitated media, and is linking the mass transfer coefficient of the quartz and the energy of the fluid. The resulting additional DSi flux due to the wave effect (1 m height in average) could double the present flux of DSi to the ocean. This work, presented at the Goldschmidt, Paris 2017 is under revision at Frontiers. The same experiments were conducted with other pure minerals, representative of the continental crust composition (anorthosite, pyroxene, olivine). We analyzed most of the elements between the masses 23 (Na) and 208 (Pb) composing these minerals. Isotopic compositions of Si and Ni (which oceanic isotopic budget is still not understood) were also determined on the same aliquots (Figure 2). The DSi dissolution kinetic under turbulent conditions and in freshwater (top left) reflects that DSi is more released in the order pyroxene, olivine and anorthosite, consistent with the solubility of the 3 minerals. Regarding the DN_i concentrations (top right), the 3 curves show a rapid increase and then a marked decrease due to the formation of secondary phases, confirmed by the DRX analyses of the secondary phases collected onto the surface of the grains. Regarding the isotopic results (bottom figures), arrows are indicating the initial isotopic signatures of each minerals for both tracers. The most striking features are i) for DSi (left), the rapid dissolution is releasing light Si, but almost simultaneously the secondary phase formation is making the solution heavier while the concentrations are still indicating release (dissolution) or reaching a plateau (which means dissolution equilibrated with precipitation, top left); for DN_i (right), the dissolution is also releasing light DN_i and the precipitation of secondary phases enriching the solutions in heavy Ni. We are currently modeling this simultaneous dissolution/precipitation for both concentrations and isotopic composition (which is very challenging) using a Monte Carlo approach. These works conducted by N. Estrade (RTRA post doc) was presented at the Goldschmidt conferences of Yokohama (2016) and Paris (2017).</p>		

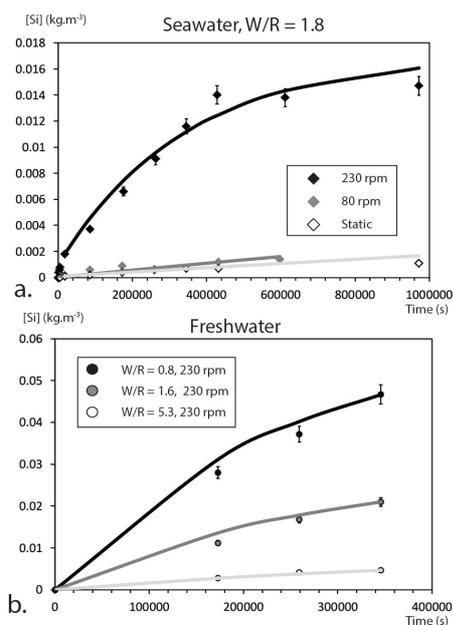


Figure 1

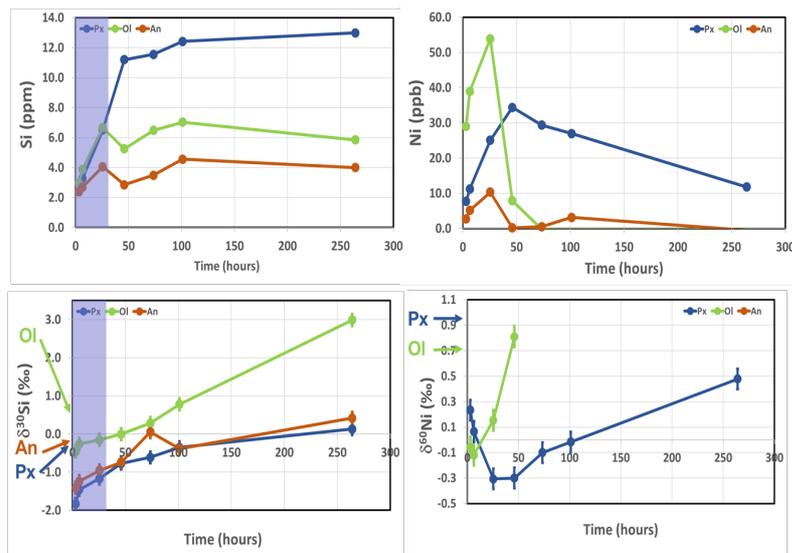


Figure 2

Figure 1: Experimental results for sand grains dissolution at various rotation speeds. (a) Silica concentrations in seawater. (b) with different W/R ratios

Figure 2: Experimental results showing the dissolution kinetics of Si and Ni under agitated conditions (230 rpm) for pyroxene (blue), olivine (green) and anorthosite (brown) in freshwaters. The top figures represent the evolution of the concentrations with time, while the bottom figures represent the isotopic compositions. The DNi released by the anorthosite was not concentrated enough to allow the measurement of the isotopic ratios.

Future of the project :

Iron concentrations and isotopes are currently analyzed on the same aliquots of the second experiment (F. Lacan, post doc of J. Klar). In addition, we would like to test the hypothesis of a “missing DSi flux due to the wave surf” on a specific adapted field (sand beaches, waves, accessible...). Discussions with D. Cardinal (LOCEAN), E. Machu (IRD Dakar) and T. Gorgues (modeling) during the LEFE days (Clermont Ferrand, 2018) could yield a LEFE/EC2CO new application to develop these ideas off selected coasts in a near future.

Communications

Estrade N., S. Fabre, G. Quitte, T. Zambardi, N. Yin, C. Cloquet, A. Probst, and C. Jeandel Experimental dissolution of lithogenic material into freshwater and seawater *Intl Goldschmidt Conf. Yokohama, 2016* POSTER

Estrade N., S. Fabre, C. Cloquet, A. Probst and C. Jeandel Isotopic and modelling constraints on experimental dissolution of lithogenic material *Intl Goldschmidt Conf. Paris, 2017* POSTER

Fabre, S., Zambardi, T., Roustan, M., Almar, R. and Jeandel, C. (2017) Clastic coasts: an overlooked term of the geochemical Si cycle? *Intl Goldschmidt Conf. Paris, 2017* POSTER

Articles

Fabre, S., Zambardi, T., Roustan, M., Almar, R. and Jeandel, C. (2019) An overlooked silica source of the modern oceans: are sandy beaches the key? **In revision, *Frontiers in Marine Science*, 2019.**

Estrade N., S. Fabre, G. Quitte, T. Zambardi, N. Yin, C. Cloquet, A. Probst, and C. Jeandel Isotopic and modelling constraints on experimental dissolution of lithogenic material **In prep. for *Nature Geoscience*, 2019.**

Deux post docs: Nicolas estrade (RTRA) et Jessica Klar (GEOVIDE et UFT) bénéficient de ces expériences.

Master 2 2017: Katia Yefsah a appliqué la même méthode sur les phases lithogéniques « a priori réfractaires » de sédiments naturels de la Rivière Têt, démontrant une libération significative d'éléments chimiques en milieu agité.