Low oxygen events in the Laurentian Channel during the Holocene

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Recent warming in the Laurentian Channel bottom water has been observed in the St. Lawrence Estuary [1] and Gulf [2]. This warming might be linked to an enhanced proportion of warm Atlantic water entering the Laurentian Channel and could be the main cause of the year-round hypoxia observed during the last 30 years in bottom waters of the lower Estuary. We observed a temperature trend of similar amplitude in a low sedimentation rate box-core located in the Esquiman Channel. Warm bottom waters conditions, however, are not exclusive to the recent time interval as shown by data from the lower part of the core, which is also characterized by low δ^{18} O values in *Globobulimina auriculata* and occurrence of both Brizalina subaenariensis and Oridorsalis umbonatus. Such data suggest the existence of low-oxygen and high temperature conditions in the bottom water of the Esquiman Channel 6-4 ka ago. These conditions are likely related to the inflow of Atlantic water in the Gulf of St. Lawrence through the Cabot Strait and the Laurentian Channel, possibly linked to large scale ocean circulation changes in the northwest North Atlantic. Hence, our results highlight the sensitivity of bottom water properties in the Gulf of St. Lawrence to North Atlantic circulation patterns.



Figure 1: Abundance of *B. subaenariensis* and *O. umbonatus* (%), calcium carbonate dissolution index (logarithm of the foraminifer linings vs shells ratio) and oxygen isotope composition in *G. auriculata* against depth in core CR06-TCE.

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Adding uptake kinetics and surface entrapment to geochemical models

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Experimentally measured trace element partitioning between a host mineral and the aqueous solution often depends on precipitation or recrystallization rates and is frequently irreversible, as shown by the occurrence of zoned crystals. Kinetic-dependent trace element uptake can be realistically simulated using partial-equilibrium aqueous- solid solution (sorption) thermodynamic models. This means that in a reaction-path sequence of equilibrium states, some amounts of relevant phases, end members, or sorbed species must be declared metastable according to time-dependent kinetic rate laws.

In this context, we considered three uptake kinetics models: Growth Entrapment (GE) [1], Surface Reaction (SR) [2], and Adsorption – In-Diffusion (AD) [3]. Each model predicts a final metastable solid-aqueous distribution of trace elements or isotopes. However, different mechanisms and parameters are invoked: the competition between mineral growth and near-surface diffusivity (GE); purely kinetic laws for gross forward and backward reaction rates for host and trace components (SR); or diffusion of trace component into the solid (AD). All models can adequately describe the trace element uptake (Fig.1) for single element/host mineral pairs (Sr/calcite, Ra/barite, P/goethite) under simplifying assumptions, such as the constancy of growth rate and of the aqueous composition.



Fig 1.: Sr distribution coefficient in calcite vs precipitation rate.

In order to make them applicable in geochemical reactive transport simulations, these models are currently implemented in the GEM-Selektor code (http://gems.web.psi.ch) in integrated forms that control time-step-dependent metastability constraints in the Gibbs energy minimization algorithm [4]. This tool can also account for changes in solid and aqueous chemistry that may occur upon the uptake in a closed system (e.g. from pore solution), while keeping track of surface areas of minerals during growth or dissolution.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement n° 269688.

[1] Watson (2004) *GCA* **68**, 1473-1488. [2] DePaolo (2011) *GCA* **75**, 1039-1056. [3] Barrow (1983) *J. Soil Science* **34**, 733-750. [4] Karpov et al. (2001) *Geochem. Internat.* **39**, 1108-1119.