

Validating geochemical models with isotopic data

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Numerical models are widely used to simulate biodegradation of organic contaminants. These models often involve complex redox conditions and degradation pathways. There is also a need to provide several degradation constants that are often poorly characterised in the field.

In order to verify the assumptions of numerical models, and the used parameters, we suggest to use isotopic data as an independent validating variable. The degradation constants used in the models are combined with laboratory enrichment factors to simulate plumes of light (^{12}C) and heavy (^{13}C) substances. The spatial distribution of the isotope ratio of each pollutant is calculated directly from the concentrations of light and heavy isotopes.

As an example we selected one of the few sites where numerical simulation were done and isotope data were measured : the Dover site (USA). The isotopic data are given only for PCE and TCE and show significant but small changes at only few points [1]. We compared a simulation done by Clement *et al.* [2] and a simulation done with our approach called MIKSS [3]. After a fitting procedure, both models are able to nicely reproduce the spatial distributions of PCE, TCE, cDCE and VC for a source active since 40 years. However as both model show some quite different degradation constants, the future evolution of the plumes will differ among the models. The simulated isotopic data are completely different between both models, with the MIKSS approach being much closer to field results than the simulation by Clement *et al.* In fact, in the MIKSS approach the degradation of the chlorinated products occur in a very small zone while it is supposed to occur over the whole plume for the Clement *et al.* model. This large zone of degradation produces a very important increase of $\delta^{13}\text{C}$ values, that does not exist in the field.

This work has also important consequences on the the treatment techniques that may differ according to the degradation hypotheses. Simulations at other sites, without $\delta^{13}\text{C}$ data, but with electron acceptors maps, show that very reduced degradation cores are the predominant pattern.

[1] Sherwood-Lollar *et al.* (2001) *Env. Sci. Technol.* **35**, 261-269. [2] Clement *et al.* (2000) *J. Contam. Hydrol.* **41**, 113-140. [3] Atteia *et al.* (2007) *Env. Sci. Technol.* **42**, 3289-3295.

The role of degassing processes on the helium paradox

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It has been observed that some OIB have a lower He content than MORB. This seems to be in contradiction with the observation that OIB have a more primitive and comparatively higher $^3\text{He}/^4\text{He}$ ratio than MORB. This has been named the helium paradox. Many hypotheses have been proposed to explain this observation. Recently, non-equilibrium degassing have been proposed to be the key mechanism responsible for the lower He content in OIB than in MORB [1].

Based on published data on Loihi and new data from Pitcairn and Society hotspots, I show that all measured OIB show equilibrium degassing with respect to major volatiles (a CO_2 and H_2O dominated gas phase). I show that a non-equilibrium degassing model such as the one presented by Gonnermann and Mukhopadhyay (2007) [1] cannot be applied to Loihi and OIB basaltic glasses. This can be easily explained by a larger initial volatile content in OIB than in MORB. A higher volatile content results in a higher vesicularity in OIB than in MORB (i.e., a larger contact surface area between the gas phase and the melt, promoting equilibrium between the two phases).

After a complete examination of possible processes that may decrease the volatile content of quenched submarine OIB and MORB glasses, I identify a combination of three processes that are at the origin of the preferential He depletion in OIB than in MORB: (1) open system degassing, (2) the vesicle bursting effect occurring during sampling and sample preparation, and (3) the post-eruptive preferential helium diffusion loss from high vesicularity OIB glasses than from low vesicularity, more massive MORB glasses.

Based on existing data, I show that it is not possible to demonstrate that OIB sources have less helium than the MORB source.

[1] Gonnermann & Mukhopadhyay (2007) *Nature* **449**, 1037-1040.