

High $^{36}\text{Cl}/\text{Cl}$ ratios and non reactive transport in Chernobyl groundwaters

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Introduction

To reduce radiation exposure rates at the site and prevent atmospheric resuspension of radionuclides (RN) released by the Chernobyl reactor 4 explosion (april 1986), about 800 trenches were dug on site to dispose contaminated material: debris, organic matter and topsoil containing reactor fuel particles. Since 1999, the CPS (Chernobyl Pilot Site) project was set up to study the migration of radionuclides from one of these trenches, the trench T22, through the unsaturated and saturated zone. A plume of ^{90}Sr was identified downstream from the trench [1]. The fate of buried RN and migration processes hence needs to be characterised. The aim of this study is to investigate processes governing non-reactive transport from the trench to the groundwater by studying the behaviour of a conservative tracer: ^{36}Cl .

Results and discussion

Significant ^{36}Cl contamination of the groundwater was demonstrated [2] with $^{36}\text{Cl}/\text{Cl}$ ratios approximately 10^3 to 10^4 higher than the theoretical natural ratio. New measurements have been performed to complete the dataset. The main source of ^{36}Cl in groundwater is most likely ^{36}Cl from the trench however other ^{36}Cl sources are probable which origins may be: (i) residual contamination after site clean-up and (ii) contamination from upstream trenches. Mixing processes are shown between these two sources. These observations lead to a conceptual non-reactive transport model in the groundwater, which includes the results of previous studies on recharge and groundwater flow system [3][4].

This conceptual non-reactive transport model will be quantitatively tested using the chemistry-transport Hytec code [5]. In a second stage, this model will be considered as a basis to investigate reactive transport for major elements, U and Sr.

[1] Dewiere (2004) *Journal of Environmental Radioactivity* **74**, 139-150.

[2] Roux (2011) *Mineralogical magazine* **75** (3), 1760.

[3] Bugai (2011) *Applied Geochemistry*, in press.

[4] Le Gal La Salle (2011) *Applied Geochemistry*, in press.

[5] van der Lee (2003) *Computers and Geosciences* **29**, 265-275.

Coupled Fe and S-isotope composition of sedimentary pyrite: Implications for Precambrian ocean chemistry and isotope biosignatures

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The rise of atmospheric oxygen level at ca. 2.3 Ga have led to dramatic shifts in the Fe-C-S oceanic cycles. Past studies of the Fe and S isotope record in sedimentary sulfides over geological time have placed important constraints on the evolution of the Precambrian ocean chemistry. Since the biogeochemical cycles of Fe and S are closely coupled in marine systems, Fe-limitation and S-limitation for pyrite formation in black shales should leave a coupled imprint on the isotopic record of both elements.

Here, we investigated the fine scale variations of Fe and S isotopic compositions of diagenetic pyrite nodules in several Devonian, Paleo-proterozoic and Archean black shales in order to (1) explore potential biosignatures using co-variations of Fe- and S-isotopes at the grain-size scale; (2) assess potential diagenetic effects on Fe-isotope fractionation during sulfide formation; and (3) assess potential mixing between isotopically distinct pools of Fe and S using multiple S isotope data. Results show that Devonian pyrite display a range of 50‰ in $\delta^{34}\text{S}$ values whereas $\delta^{56}\text{Fe}$ values vary between -1.0 and +0.1‰ consistent with Fe isotope variations in modern marine sediments. Similarly, pyrite in the 1.88 Ga Gunflint Formation has $\delta^{34}\text{S}$ values ranging from -32‰ to +10‰ and displays a range of $\delta^{56}\text{Fe}$ values between 0 to -0.4‰. In contrast, Archean black shales display a smaller range of $\delta^{34}\text{S}$ values between -5 and +18‰ but a larger range of $\delta^{56}\text{Fe}$ values from -3.5 to +0.2‰. A transitional period between 2.3 and 1.8 Ga is marked by a larger spread of $\delta^{34}\text{S}$ values from -34 to +28‰ and a larger range of $\delta^{56}\text{Fe}$ values from -1.7 to +1.1‰. These results confirm that after the rise of atmospheric oxygen, the Paleoproterozoic ocean became stratified and gradually affected by an increase of sulfate concentration in an Fe-limited system whereas pre-2.3 Ga ocean was S-limited and characterized by extensive Fe-oxide precipitation and redox cycling. This transition was also linked to profound changes of microbial processes, diagenetic conditions, and Fe redox cycling, that are all ultimately linked to the evolution of the global ocean chemistry.

We also investigated the chemolithostratigraphic variations of Fe-isotopes and Fe speciation in order to establish an Fe isotopic mass balance in black shales and its relation to environmental conditions. All together, our results confirm the existence of an isotopically negative, anoxic, Fe-rich seawater pool before 2.3 Ga, which may be in part fueled by dissimilatory Fe reduction as well as hydrothermal input. Regardless of potential Fe sources, light Fe isotope signatures in Archean and Paleo-proterozoic oceans are consistent with partial Fe oxidation in the photic zone, leading to the precipitation of isotopically enriched Fe-oxides and fueling extensive microbial Fe cycling.