

## Ocean oxygenation during the PETM: Mo isotope data from the Arctic and Tethyan Oceans

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Evidence for ocean deoxygenation during past intervals of global warming can help to set observations of expanding oxygen minimum zones in the modern oceans into a longer term geological context. The molybdenum (Mo) isotope composition of the hydrogenous Mo in marine sediments that accumulated in euxinic settings can preserve the seawater Mo-isotope composition, which in turn reflects the balance between oxic, anoxic, and euxinic sinks in the global ocean. As such, it can be used to determine the extent of deoxygenated waters in past oceans when the local depositional environment is well characterised. We present new Mo isotope data of samples from Arctic Ocean IODP Site 302 and from continental shelf sites on the northern Tethyan margin (Guru-Fatima and Kheu River) that accumulated during the Paleocene-Eocene Thermal Maximum (PETM) ~56 Ma ago. The PETM is characterised by a global C-isotope excursion (CIE) caused by the introduction of a large amount of isotopically depleted carbon into the earth-ocean-atmosphere system, which in turn caused global temperatures to rise by 5-8°C.

Mo isotope data from IODP Site 302 broadly mirror the organic carbon isotope excursion recorded in the same sample suite, with near uniform values of 2.1 ‰ during the peak of the CIE and lower values during the late Paleocene and during the PETM recovery interval. Samples that accumulated during the peak of the CIE were deposited under locally euxinic conditions, demonstrated by trace element data measured in the same samples and also by comparison to published organic geochemical data. Their Mo-isotope values consequently record the seawater value at this time, which was only ~0.2 ‰ lower than modern seawater (~2.3 ‰). This finding suggests that (1) once euxinia in the Arctic Ocean is accounted for, global ocean anoxia was not widespread during the PETM and (2) the Arctic ocean was unrestricted during the PETM. In contrast, preliminary Mo isotope data from the northern Tethys Ocean suggest a slight expansion of ocean anoxia at the onset of the CIE, an interval that is missing within the Arctic core.

## Hydrogen sorption by synthetic montmorillonites and clayrock at high temperature

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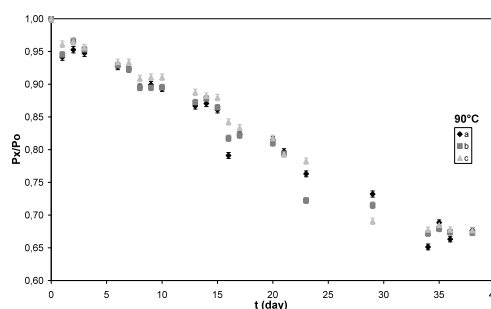
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Hydrogen is more and more studied as a future energy carrier due to its availability and its energy capacity. The montmorillonite clay minerals are recognized as good hydrogen adsorbents [1] due to their large specific surface area and their wide range of porosity. In addition to this application, a clayrock has been considered as a host rock for French nuclear waste and particularly the Callovo-Oxfordian (COx), principally constituted by smectite and illite clays. Regarding nuclear waste repository, hydrogen gas is expected to develop from the anaerobic corrosion processes of the waste containers after the disposal closure. It is therefore of fundamental importance to study the fate of the hydrogen gas produced in the system, in terms of reactivity and integrity of the surrounding claystone layer.

This study aims at investigating hydrogen sorption on different types of synthetic montmorillonites and COx clayrock using gas chromatography and Sievert technology. Two-month long experiments were carried out at 90°C (the maximum temperature in the waste repository site) with dried or saturated clays. The hydrogen partial pressure varies from 0.1 to 0.45 bars.

Dried experiments show a sorption of hydrogen amount of 0.13 wt%. Experiments with saturated clays highlight a decrease of headspace hydrogen pressure (the figure below) as a function of time for a COx powder in NaCl aqueous solution taking into account the dissolved hydrogen. Sievert technology using high pressure of pure hydrogen gas (up to 80 bars) at 90°C shows a maximum sorption of 0.20 wt% for synthetic montmorillonite and 0.16 wt% for COx sample.



**Figure 1:** Evolution of hydrogen relative pressure with time for clay fraction of a COx sample at T = 90°C

[1] Gil, A. *et al.* (2009) *International Journal of Hydrogen Energy*, **34**, 8611-8615,