

## Impact of authigenic particles on phosphate and trace metal budgets of anoxic basins

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Intense element cycling causes steep gradient of nutrients and redox-sensitive trace metals at pelagic redoxclines; the transition zone separating oxygenated surface waters from sulphidic bottom waters. Besides well-known Mn-oxides, SEM-EDX inspection of authigenic particles from the redoxcline of the Black and Baltic Seas evidence existence of postulated Fe-phosphates as well as mixed phases comprising Mn, Fe, and P as a new solid species (Mn-Fe-P shuttle). Throughout the redoxcline, these minerals show a general succession with maximum abundance of Mn-oxides above the redoxcline followed by mixed phases and almost pure Fe-phosphates within and below the redoxcline. Morphological similarities and molar Fe/P ratios suggest the formation of irregular Fe-oxyhydroxo coatings on sinking MnO<sub>x</sub> particles followed by immediate adsorption of phosphate. Despite oxidation by O<sub>2</sub>, batch-type experiments using biogenic Mn-oxides demonstrate the efficient potential of Fe<sup>2+</sup> oxidation by sinking MnO<sub>x</sub> particles. When entering sulfidic waters MnO<sub>x</sub> is further reduced, thus causing an increasing relative abundance of Fe-phosphate. We suggest a conceptual model for the Mn-Fe-P shuttle at pelagic redoxclines, which affects phosphate transport throughout the water column and thus impacts primary production at least over longer time scales. This Mn-Fe-P-shuttle likely played an important role for the cycling of P in ancient ocean basins, e.g., during certain periods of Cretaceous black shale formation and should be considered in future modelling approaches dealing with stratified ecosystems. Furthermore, this shuttle influences the cycles of certain trace metals via scavenging. High-resolution determination of trace metals in sapropelic sediments from the Gotland Basin (Baltic Sea) will be compared with the elemental composition of authigenic particles from the water column in order to assess preferential enrichments in the sedimentary record.

## Li content and isotopic distributions in granulite of Kerguelen plateau

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Kerguelen basalts contain abundant mantle xenoliths, including mantle peridotites and deep magmatic segregates equilibrated in the granulite facies [1]. Lithium chemical and isotopic distribution were measured in two-pyroxene granulites, in order to define their signature and describe the Li behavior during the lower crust formation processes. Li content and isotopic composition were measured in using the Cameca IMS 1270 Ion probe at CRPG, with reference Cpx and Opx with compositions close from those of the samples.

The studied xenoliths display close mineralogical compositions, bearing Mg81-92 Al-diopside, Mg-78-93 enstatite and labradorite or bytownite. Spinel and garnet are observed in 2 of them, and they all are type II xenoliths [1,2]. On the whole rock scale the Li contents range from 1.5 up to 9 ppm, with Li content decreasing from Cpx to Opx with a ratio Opx/Cpx of 0.8-0.9 and a ratio Plag/Cpx of 0.2-1. At the grain scale, Li displays a homogeneous distribution, at the exception of depleted or enriched Cpx rims. Only the more Li depleted sample display heterogeneous Li distribution in both Cpx and Opx.

The  $\delta^7\text{Li}$  values measured on Cpx and Opx range between +4 and +14, with most of the values between +5 and +8. The cpx depleted or enriched rims display  $\delta^7\text{Li}$  values associated to Li diffusion. Only the Li poor xenolith display  $\delta^7\text{Li}$  values scattered on a large range, from -9 to +14. A general observation is that Cpx display rather slightly higher  $\delta^7\text{Li}$  values than Opx, and those values are more scattered in Opx than in Cpx. The  $\delta^7\text{Li}$  values for Plag are in progress and will be presented, but could not affect a lot the Li isotope budget, are most of Li is beard by Opx and Cpx.

The bulk value for these granulite samples is in agreement with a direct derivation from the mantle (5-8 ppm,  $\delta^7\text{Li} \approx +5$ ). But their Li content is lower than expected for the lower continental crust [3], suggesting that Li in the lower continental crust is not mainly derived from the mantle.

[1] Gregoire *et al.* (1998) *Contrib Mineral Petrol* **133**, 259-283. [2] Gregoire (1994) PhD thesis. [3] Rudnick and Gao (2004) *Treatise on Geochemistry* **3**, 1-64.