

## Which trivalent phosphate controls acidic surface water P availability?

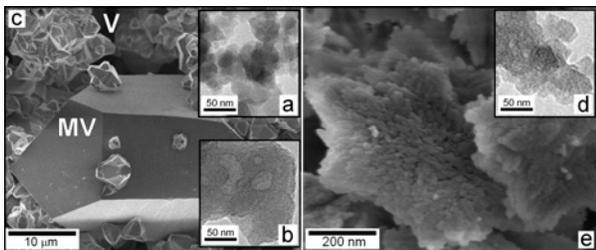
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Phosphate concentrations in natural waters have been of increasing concern because if they are too low they may hinder forest and agricultural growth, but if they are too high they may lead to eutrophication [1]. Thermodynamic calculations suggest that the Al and Fe phosphates, variscite and strengite, control aqueous phosphate concentrations in acidic (pH<7) environments [2]. This study is aimed at assessing experimentally the role of these minerals in controlling phosphate availability in natural waters.

The formation and dissolution of Al and Fe-phosphate phases were investigated experimentally at 25°C to 200°C and 1.5<pH<9. Solids were characterized by XRD, FTIR, FEG-SEM and HR-TEM, and Al, Fe, and P in solution were analysed by ICP-AES, IC and UV-Vis. Batch reactor experiments show that Al and Fe phosphate phases readily precipitate from supersaturated solutions. Precipitation is initiated by the nucleation and growth of amorphous Al or Fe phosphates (AAP and AFP, respectively). At T=100°C the amorphous phosphates recrystallize into either variscite (V) and metavariscite (MV), or strengite, respectively. At lower T, amorphous phosphates persist for at least several months. Dissolution experiments demonstrate these phases rapidly dissolve in undersaturated solutions. These results suggest that amorphous Al and Fe phosphates limit P availability in many natural environments.



**Figure 1:** Photomicrographs of (a) AAP at t=0, (b) AAP at t=12 days; (c) MV and V at t=21 days at 100°C; (d) AFP at t=0 and (e) strengite crystals at t= 5days at 100°C.

[1] Oelkers and Valsami-Jones (2008) *Elements* **4**, 83-87.

[2] Stumm and Morgan (1996) *Aquatic Chemistry*, John Wiley and Sons Inc., New York.

## REEs in authigenic carbonates: A new proxy for tracing fluid sources at cold seeps

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At cold seeps, authigenic carbonates form as a result of the microbial oxidation of methane and, hence, represent suitable archives of fluid seepage on continental margins. Here, we have investigated the potential of using REEs in authigenic carbonates for tracing fluid sources at cold seeps, and providing additional constraints on associated biogeochemical processes. A series of carbonate samples was analysed, collected from various active sites of fluid venting, and characterised by distinct mineralogical compositions. These samples were recovered from the Niger Delta area over the past few years [1], during several expeditions funded by IFREMER and TOTAL (NERIS and ERIG-3D projects).

The samples were leached with 5% acetic acid, and analysed by SF-ICP-MS (ELEMENT II) after Tm addition [2]. They exhibit a wide range of shale-normalised REE patterns. Most aragonite concretions recovered from hydrate-rich pockmarks display very similar patterns (e.g. distinct MREE bulge), but their total sum of REEs ( $\Sigma\text{REE}_N$ ) vary significantly from one sample to another. In contrast, high-Mg-rich samples are characterised by similar  $\Sigma\text{REE}_N$  contents, but display a wide range of REE patterns. A few siderite concretions recovered from a mud volcano exhibit much higher REE concentrations. Taken together with additional data for stable isotope ratios and REEs in selected pore water samples, these results will be discussed to provide constraints on the factors controlling REE distribution in cold seep carbonates.

[1] Bayon *et al.* (2007) *Mar. Geol.* **241**, 93-109. [2] Bayon *et al.* (2009) *Geostand. Geoanal. Res.* **33**, 51-62.