Modelling past and present phosphate cycling off Peru

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The burial of phosphorus and the formation of phosphorites (phosphogenesis) in marine sediments represent an important sink in the global phosphorus cycle. Today, neither the source of phosphate of massive phosphorite deposits nor the formation mechanism of phosphate minerals are known with certainty. To elucidate this further, we performed hydrogeochemical modelling on ODP sites (Leg 112 and 201; D′Hondt et al., 2002; Suess et al., 1988) along a transect from the shelf to the lower slope off Peru. We investigate the recent situation as well as phosphorus cycling in the Miocene. Our modelling tool is the PHREEQC (version 2) computer code (Parkhurst and Appelo, 1999).We model interdependent diagenetic reactions evolving into a diffusive multi-component and multi-phase system by means of thermodynamic equilibrium calculations of species distribution. Reaction kinetics of organic carbon conversion is integrated into the set of equilibrium reactions by defining the type and the amount of converted organic matter in a certain time step. The model setup describes a growing sediment column. One-dimensional molecular diffusion of aqueous and gaseous species as well as burial of solids and aqueous species are considered.

Formation of carbonate fluorapatite (CFA) is difficult to model because of different elemental composition with unknown thermodynamic constants. For that reason different approximations are modelled. We chose four different CFA compositions, however same equilibrium constants were attributed to all of them: i) FCO3Apatite, containing 2.48 mol fluoride ($Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{4.8}(CO_3)_{1.2}F_{2.48}$), that is defined in the database of PHREEQC, ii) a CFA composition without fluoride ($Ca_{9.316}Na_{0.37}Mg_{0.144}(PO_4)_{5.63}(CO_3)_{1.2}$), iii) a CFA with 0.68 mol fluoride ($Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{5.4}(CO_3)_{1.2}F_{0.68}$), and iv) a CFA with 0.98 mol fluoride ($Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{5.3}(CO_3)_{1.2}F_{0.98}$).

The more fluoride is incorporated in the mineral phase, the less CFA formed according to model calculations. Fluoride diffusion from the sea water into pore waters seems to be important and, consequently, sedimentation rates strongly influence model results. Model results indicate CFA formation in the upper part of the sediments with highest organic matter conversion. Exceptional is the lower slope site 688. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) formation takes place due to very high organic matter conversion in Holocene/Pleistocene sediments that leads to high ammonia concentrations in pore water. CFA formation is negligible at this site.

Calculations of phosphate fluxes from sediments into overlying bottom water show higher values (one order of magnitude) from slope sediments compared to shelf sites, at present day. In the Miocene, present day lower slope sites are located at a former shelf underneath an upwelling cell. The phosphate flux from these sediments in the Miocene was one order of magnitude lower compared to the recent situation and is comparable to the flux of present day shelf sites. Thus, shelf environments seem to be most important when investigating phosphate cycling and storage in marine environments.

However, modelled amounts of authigenic CFA in Peruvian shelf sediments are lower compared to measured contents (Jaisi and Blake, 2010). Additional mechanisms have to exist that enrich phosphate in pore waters close to the sediment/water interface and increase CFA precipitation. Possibly bacteria are involved in such processes (e.g. Arning et al., 2009). Furthermore, winnowing and erosion due to bottom currents may lead to phosphate mineral enrichment, but these processes are not included in our model calculations, so far.

Arning, ET, Birgel, D, Brunner, B, Peckmann, J (2009) Geobiology, 7, 295-307.
D′Hondt, SL, Jørgensen, BB, et al. (2002) Proc. ODP, Initial Reports, 201, College Station, Texas.
Jaisi, DP, Blake, RE (2010) GCA, 74, 3199-3212.
Parkhurst, DL, Appelo, CAJ (1999) USGS, Water resources investigation report 99-4250, Denver, Colorado, 312 p.
Suess, E, von Huene, R, et al. (1988) Proc. ODP, Initial Reports, 112, College Station, Texas.