Redox dependent phosphorus cycling: Microbial and abiotic processes

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The geochemistry of phosphorus (P) has received considerable attention because of its role as an important nutrient in both marine and freshwater systems. Dissolved P concentrations often increase dramatically at oxic-anoxic transitions in water columns and sediment pore waters. The most commonly invoked mechanism to explain this increase is based on the large sorptive capacity of ferric oxyhydroxide particles for phosphate. Reductive dissolution of these particles results in regeneration of not only Fe(II), but also associated phosphate. Recent calculations reveal that the P regeneration attributable solely to this mechanism may be insufficient to account for enhanced benthic P fluxes observed in anoxic environments (Ingall and Jahnke, 1997). Another mechanism, commonly overlooked but potentially significant, is the storage and release of P associated with the redox sensitive production and consumption of intercellular polyphosphate by certain microorganisms. Yet another potential mechanism is release of P sorbed to particulate Mn oxides during reductive dissolution of those Mn oxide particles. Here we present preliminary evidence from the oxic-anoxic transition zone of a stratified marine basin and show that redox sensitive mechanisms, in addition to the regeneration P from iron oxyhydroxides, play a key role in P cycling.

Study site

The Orca Basin is a bathymetric depression at a depth of approximately 2400 m on the continental slope of the north-central Gulf of Mexico. The lower 180m of the basin is filled with a brine, which has a salinity about 7.5 times higher than average seawater. The pronounced density contrast of the seawater-brine interface restricts vertical solute exchanges between the brine and the overlying seawater, thus the brine remains permanently anoxic. Two advantages of studying the Orca Basin are the large spatial scale and stability of the chemocline. Redox processes normally occurring over spatial scales of a few centimeters in sediments are spread over 40 m of water column, which allows for fine-scale sampling within particular redox zones. Available water column temperature, salinity and other profiles from the earliest cruises in the late 1970's are comparable to data from our recent 1996 cruises. Thus, the water column chemistry of the Orca Basin appears to be close to steady state, at least on decadal time scales.

Sampling and methods

Data presented in Figs. 1 and 2 were gathered during three cruises in April, September and November of 1996. Water samples were collected using 12L Niskin bottles mounted on a CTD rosette. Samples were withdrawn from Niskin Bottle outlets using polypropylene syringes and were then filtered through 0.45 μm polypropylene Puradisc filters. Samples for dissolved metal and phosphate analysis were immediately acidified to pH 1 with high purity trace metal grade HCl. Dissolved oxygen concentrations were measured directly by an oxygen electrode incorporated into the CTD system. Because the salinity of the brine was beyond the conductivity range of the CTD, the seawater-brine interface was characterized using chlorinity determined by silver nitrate titration. Dissolved phosphate, ammonium, Fe(II) and Mn(II) concentrations were determined spectrophotometrically.

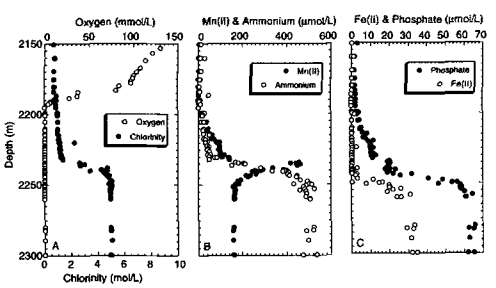

FIG. 1. Water column concentration profiles focusing on the redox transition of the Orca Basin.

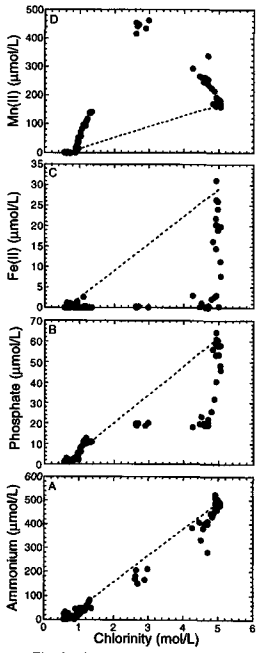

FIG. 2. Mixing diagrams. Dashed lines represent conservative mixing.

Results and discussion

Profiles of dissolved oxygen, chlorinity, Mn(II), ammonium, Fe(II), and phosphate concentrations are shown in Fig. 1 for the Orca Basin water column focusing on the depth range where the major transitions occur. Oxygen (Fig. 1A) and nitrate (not shown) concentrations decrease to zero at approximately the same depth where chloride concentrations (Fig. 1A) and hence, water density begins to increase. The decrease in oxygen and nitrate is consistent with accumulation and subsequent oxidative degradation of organic-rich particles in the strong pycnocline coupled with the restricted transport of oxygen and nitrate across the density contrast. When oxygen and nitrate are depleted, marine heterotrophic bacteria sequentially use Mn oxides, Fe oxyhydroxides and sulphate as electron acceptors for organic carbon respiration. This utilization of oxidized Fe and Mn phases as electron acceptors is reflected in the large increases in dissolved Mn(II) and Fe(II) concentrations at 2235 and 2250 m (Fig. 1B and 1C).

Figure 1 shows that dissolved phosphate concentrations start increasing above ambient bottom water values at 2190 m, the depth where oxygen concentration goes to zero. Dissolved phosphate concentrations increase steadily for the next 55 m and then increase dramatically at 2245 m, coincident with the large increase in dissolved Fe(II) concentrations. The increase in phosphate concentrations in the region where dissolved Fe(II) concentrations are zero indicates that a portion of phosphate regeneration is not associated with the reductive dissolution of Fe oxyhydroxides. There are several potential mechanisms for this increase, namely release of phosphate associated with 1) organic matter trapped in the pycnocline, 2) Mn oxides, and 3) redox-dependent polyphosphate metabolism in microorganisms.

To differentiate between the above possibilities and to highlight zones of production or consumption, ammonium, phosphate, Fe(II) and Mn(II) concentrations are plotted against chlorinity in a mixing diagram in Fig. 2. In such a diagram, concentrations of conservative species lie on a straight line between end member seawater and brine concentrations. Curvature in the concentration versus chlorinity profile reflects production (concave-up) or consumption (convex down). Inspection of Fig. 2B shows that there is a zone of dissolved phosphate production between chlorinities of approximately 1 and 4 mol/L. Figure 2C indicates that Fe(II) is consumed at chlorinities less than 5 mol/L. Hence production of dissolved phosphate between chlorinities of 1 and 4 mol/L cannot be related to dissolution of iron oxyhydroxides. Production of phosphate in this zone does not coincide with any indication of enhanced ammonium production (Fig. 2A), suggesting that the release of phosphate in this zone is not associated with organic matter decomposition in the pycnocline.

The lower chlorinity zone of phosphate production approximately corresponds with the zone of peak Mn oxide reduction (Fig 2D). Unfortunately, polyphosphate metabolism occurs at nearly the same redox potential as Mn oxide reduction (Davelaar, 1993), thus determination of the exact origin of phosphate in this zone is difficult. However, polyphosphate metabolism is consistent with indications of large and active microbial populations, which are inferred from highly elevated adenosine 5'-triphosphate concentrations and extremely high uridine uptake rates at the depth of this zone (LaRock *et al.*, 1979). Further study is needed to assess the relative contributions of the proposed mechanisms for P cycling across redox transitions.

References

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