

# Controls on Minor Element Compositions of Early Diagenetic Siderites and Dolomites in the Mississippi River Delta Plain

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## Introduction

Early diagenetic siderites occurring in deltas contain significant and variable concentrations of minor elements. Attempts have been made to evaluate potential controls on concentrations of minor elements in sedimentary siderites (Mozeley, 1989; Mortimer et al., 1997; Rimstidt et al., 1998) and to relate them to specific environments of formation. However, few data are available for natural porewaters and associated siderites. Such data are needed to evaluate models based on studies of ancient sequences and on laboratory studies.

## Methods

Cores of structurally intact Mississippi River delta plain sediment, a marine-influenced core on the present coast and several inland cores, provided samples of pore solutions and diagenetic siderites containing accessory dolomites. After expelling pore-water solutions from the clay-rich sediments with a gas-pressured cell, samples were membrane-filtered, acidified, and analyzed for metals by ICP. Samples of siderite were located by inspection of X-ray radiographs and cut intact from cores, impregnated with epoxy, and polished thin sections produced. These thin sections were analyzed using electron-probe micro-analysis and micro-PIXE.

## Results and discussion

Pore solution compositions vary vertically in the cores and between the cores. Specifically, Fe and Mn concentrations are higher in the tops of the cores in general, reflecting reduction and solubilization of oxidized Fe and Mn compounds in the sediments, followed by precipitation of siderites with burial. Ratios of Mg/Ca are somewhat higher, and Fe concentrations lower in the coastal core than in inland cores, reflecting influx of seawater.

Mole fractions of minor elements in these siderites are around 0.1 for Ca, around 0.01 for Mg, and variable from about 0.01 to about 0.1 for Mn. Ratios of the mole fraction of Mg to the mole fraction of Ca in siderites have been used as indicators of marine versus freshwater environments by Mozeley (1987). In the present deltaic samples, these ratios do not differ much between the coastal core and inland cores and, in general, appear to be closer to the freshwater siderites given by Mozeley (1989) than his marine siderites. Concentrations of Fe in accessory dolomites, which form before most of the siderites, are higher in the inland cores, reflecting greater availability of Fe in very early porewater solutions at the inland sites.

Comparison of mole fraction ratios of minor elements to Fe in the siderites with ratios of molar concentrations in solutions suggests that Ca, Mg, and Mn are taken into the siderites in the order Mn>Ca>Mg relative to the solutions. This pattern is in approximate relative agreement with experimental nonequilibrium distribution coefficients determined by Rimstidt et al. (1998), though values obtained in the present study are generally lower than those obtained by Rimstidt et al. (1998). These distribution coefficients reflect effects of relative solubility products and rate processes.

Minor element data also show some features which may relate to microbial activity, as suggested by Mortimer et al. (1997). For example, a negative relation between the mole percent of Mn in these siderites and  $\delta^{13}\text{C}$  may reflect decreased Mn incorporation with increased microbial activity at depth. Also, Mg/Ca ratios may be affected by microbial activity during precipitation. In addition to features in minor element data, association of some very early siderites with soft tissue in remains of organisms also points towards microbial activity. Further work on microbially-mediated precipitation of siderite is needed.

## Summary

In summary, results from pore solutions and associated siderites in modern Mississippi River delta plain sediments show that Mg/Ca ratios are closer to ratios of freshwater siderites and do not appear to differ systematically with proximity to the coast in these deltaic siderites. However, there are higher concentrations of Fe in dolomites in inland cores than in dolomites in the coastal core. There is preferential incorporation of Ca relative to Mg from solution into these siderites that may reflect factors in partition coefficients or microbial effects. Mn incorporation into siderites appears to be related to microbial activity, as does association of very early siderites with soft tissue in remains of organisms. Bulk solution chemistry, factors included in inorganic experimental nonequilibrium distribution coefficients (solubility products and rate processes), and microbial activity appear to be involved in determining minor element compositions of these diagenetic siderites and dolomites.

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