Diagenetic mineral formation in sediments of the Mississippi River delta plain

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Introduction

Previous studies (Bailey et al., in review) on two 40 m borings of Mississippi River delta plain Topstratum deposits, one freshwater and one marine-influenced, show diagenetic minerals to be abundant and varied in both borings, though slightly less so in the marine-influenced boring. Included are: siderite, pyrite, calcite, dolomite, vivianite, and Fe/Mn-oxides, with siderite and pyrite being most common. These findings are similar to those described by Ho and Coleman (1969) in an earlier reconnaissance study of these sediments and similar to those reported by Postma (1982) for coastal sediments in Denmark. In addition, Curtis et al., (1986) and others describe similar diagenetic minerals for ancient deltaic sequences. Variations of siderite and pyrite concentrations with lithology, depth and marine influence were also examined. Siderite varies with lithology and depth, but not with marine influence, while pyrite varies with lithology and marine influence, but not depth. In general, siderite occurs in finer-grained siliciclastic layers of coarsening-upward sequences comprising the delta, and concentrations increase with depth to about 20 m. Pyrite is most concentrated in organic-rich horizons that cap the sediment sequences and is somewhat higher in the marineinfluenced boring.

Acquisition of a new set of two long (> 40 m)borings and three short (< 16 m) borings has allowed expansion of these studies through incorporation of pore water data and more detailed X-ray diffraction and petrographic examinations. Further, marine influence for the new borings ranges from slight for the most inland boring to a maximum (for both studies by the authors) for the southernmost of these borings, which is located on the present-day coastline of the delta.

Methods

For the new set of borings, pore water solutions were collected as soon as possible by removing 60

cc subsamples of sediment from the bottoms of sequential 1m long core sections and then expelling solutions using a gas-pressured squeezer. Solutions were filtered and separated into different portions for determination of metals by inductively coupled plasma emission spectroscopy, pH and sulphide potentiometrically, and chloride and alkalinity by titration.

Nodules were cut intact from the cores and airdried or freeze-dried. Subsamples were then taken using a 3mm core cutter and ground to < 320mesh for X-ray diffraction determinations. Another set of subsamples were cut from the nodules, impregnated with resin, sectioned, and polished. These were examined using light microscopy and scanning electron microscopy incorporating a backscattered electron detector and X-ray microanalysis.

Results

For the pore solutions from the new set of borings, Cl concentrations range from above 10,000 mg/L in the coastal boring to < 500 mg/L in the most inland boring. Dissolved Fe concentrations display maxima at depths of around 10 m and then drop to detection levels. The maximum for the coastal boring is much less pronounced. Depth distributions of dissolved Mn mimic that of dissolve Fe although absolute concentrations of Mn are lower. Both dissolved bisulphide and bicarbonate are close to the detection limits for the methods used in this study. For Ca concentrations, values are generally in the range of several hundred mg/L and are higher in the inland boring and lower in the coastal boring. Concentrations of Mg are generally lower than Ca and are higher in the coastal boring than the inland boring.

As with earlier studies, major diagenetic minerals include: siderite, pyrite, calcite, dolomite, vivianite, and Fe/Mn oxides. Compositions of nodules in the inland boring are most similar to those from the earlier borings, where siderite is the dominant mineral. However, nodules in the coastal boring are composed primarily of calcite and/or dolomite, and are generally less common than in the other borings studied.Polarized light microscopy shows that siderite nodules are predominantly composed of small (one micron) irregular siderite grains and somewhat larger colorless carbonate grains that may have rims of siderite. Mozley (1989) notes similar intergrowths in ancient nodules. Assorted clastic grains, dominantly quartz, are found in all nodules examined and are generally higher towards the margins. X-ray microanalysis indicates that the siderite generally contains appreciable Ca, as noted by Moore *et al.* (1992). Minor Mg and traces of Mn are also present.

Microscopic examination of pyrite-rich zones shows that pyrite occurs as individual octahedral crystals and spherical aggregates which fill root channels and are associated with organic fragments in siliciclastic matrices. Sizes of individual crystals are around a few microns, while diameters of spherical aggregates range from 10 to 60 microns.

Discussion

While other interpretations may be possible at this stage, pore solution data are compatible with processes suggested in previous studies. Iron profiles reflect solubilization of Fe in sediment as the sediment encounters reducing conditions. Concentrations are restricted in the coastal boring by sulphide precipitation. In the inland boring, sufficient Fe in solution passes through the sulphide reduction zone to permit later abundant siderite formation. In the coastal boring, available Fe may be precipitated as sulphides. Ca and some Mg are then used for calcite and dolomite precipitation in the absence of abundant siderite formation. In general, low values of bisulphide and bicarbonate in solution are consistent with removal through precipitation.

As in the earlier study, petrographic examinations support a model in which pyrite generally forms very early during burial diagenesis in organic-rich horizons, while siderite forms somewhat later in siliciclastic horizons. Zoning in sideritic nodules suggests changing solution compositions in the sediment.

In general, the solution and solid data indicate a coupling of chemical processes in organic-rich horizons (pyrite formation) with those in siliciclastic horizons (siderite formation). During very early formation of pyrite, Fe moves from siliclastic horizons to organic-rich horizons. During later formation of siderite, Fe is rearranged within siliclastic horizons, as indicated by elongated morphology of nodules parallel the strata. Increased calcite and dolomite accessory concentrations towards margins may indicate temporary exhaustion of available Fe.

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