Minor and trace element compositions of carbonates formed during burial diagenesis of deltaic sediments

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Studies of long cores of river-dominated Mississippi River delta plain sediments (Ho and Coleman, 1969; Moore *et al.*, 1992; Bailey *et al.*, 1998) show a varied suite of early diagenetic minerals. In general, siderite is most abundant in these sediments, followed by pyrite. These minerals vary with depth and proximity to the present coast. Pyrite and accessory calcite and dolomite appear to form early, while siderite forms later during burial diagenesis. Siderite is the predominant carbonate in inland cores and at depth in a core along the present coast. Minor calcite and dolomite are the primary carbonates present in the upper part of the coastal core.

Studies of tide-dominated Mahakam River delta plain sediments (Bailey and Roberts, 1996) show an early diagenetic suite that consists of pyrite, calcite, and siderite. Calcite predominates in shallow cores, but some Pleistocene cores show siderite that resembles siderite in onshore Mississippi River Delta cores. Concretions from the marine portion of the Rajang Delta also show calcite with minor siderite. Studies are being extended through collection of minor and trace element data for these concretions and examination of these data in the framework of the coastal setting and burial diagenesis.

Methods

Using X-radiographs as guides, diagenetic carbonates were located and cut from sediment slabs. Samples were split into two parts: one for X-ray diffraction and isotopic work and the other for a polished thin section. Polished sections were then examined by light microscopy to locate areas for further examination by electron microprobe analysis (EMPA) in the microprobe laboratory at Louisiana State University and micro-PIXE analysis in the accelerator laboratory at the University of Guelph, Canada. EMPA determinations include: CaO, MgO, FeO, and MnO. Initial micro-PIXE determinations include: Ba, Sr, Zn, Zr, Rb, Th, Ni, As, Ga, Y, Cu, and Nb.

Results and discussion

Averages for EMPA determinations are given in Table 1. CaO and MgO occur as minor constituents in siderites examined and MgO as a minor constituent in calcites examined. Siderite CaO concentrations range from 2.74% to 9.66%, while MgO concentrations range from 0.09% to 0.72%. MgO/CaO ratios are much lower than in associated porewaters, suggesting that precipitation is influenced by microbial or other factors (Mortimer *et al.*, 1997). MgO concentrations in calcite range from 0.05% to 5.55% and are generally higher in marine settings. FeO occurs as a minor constituent in calcite and dolomite. In calcite, FeO concentrations range from 0.01% to 7.73%, with high values occurring in Mahakam samples. These often consist of complex mixtures of siderite and calcite. Some values may represent contamination of the signal from associated siderite, or they may represent a genetic relationship between the calcite and siderite. FeO concentrations in dolomite range from 0.02% to 4.84% and are higher in freshwater settings than in the marine-influenced core, where Fe is tied up as sulphides during early diagenesis. Mn occurs as a minor constituent in calcite, dolomite, and siderite. Calcite and siderite concentrations are generally low and variations are not considered here. MnO in siderites ranges from 0.49% to 7.09% and appears to have a

TABLE 1. Average CaO, MgO, FeO, and MnO concentrations in siderites (31), dolomites (18), and calcites (8), determined using EMPA (all values wt.%)

	CaO	MgO	FeO	MnO
Siderite	4.77 wt.%	0.51	49.60	3.29
Dolomite	29.08 wt.%	21.10	0.90	0.16
Calcite	40.84 wt.%	3.55	3.43	2.79

TABLE 2. Initial average concentrations of trace metals in siderites (6) from the Mississippi River Delta, determined using micro-PIXE analysis. Also shown are corresponding averages for trace metals in lacustrine clays from the Mississippi River Delta, determined using XRF and ICP-MS (all values ppm)

	Ba	Sr	Zn	Zr	Rb	Th	Ni	As	Ga	Y	Cu	Nb
Siderite	284	60	36	23	15	8	8	6	5	5	4	3
Clay	680	145	117	161	129	12	28	19	17	31	33	24

negative relation with $\delta^{13}C$, i.e. higher Mn concentrations are associated with lower values of $\delta^{13}C$. Siderite is formed with progressive methanogenesis in these samples and it may be that Mn is used up as methanogenesis progresses.

Initial micro-PIXE analyses of siderite from Mississippi River delta samples gave averages shown in Table 2 for trace elements present above detection limits. Also shown in Table 2 are average concentrations of these elements for lacustrine clays from these deltaic deposits (determined by XRF and ICP-MS). Elements are arranged from highest to lowest concentration in the siderite. Two points appear from Table 2: (1) concentrations of these trace metals are lower in the siderite than in the associated sediment and (2) while ratios of concentration in siderite to that in clay vary from element to element, patterns in siderite are approximately parallel those in the clay. From X-ray diffraction data, micro-PIXE scans across a concretion, and care taken in selecting areas for analysis, it is assumed that these elements are generally in the siderite lattice. Since Fe and Mn for these concretions are released from hydrated Fe and Mn oxides during reduction and since these hydrated oxides are known scavengers for a wide variety of trace metals, it appears likely that these trace metals may have been released into solution during reduction and co-precipitated with the siderite. Lower concentrations in siderite than in associated clay suggest that only that fraction in the hydrated Fe and Mn oxides is available. Variation in ratios may reflect variations in proportions in hydrated Fe and Mn oxides.

Conclusions

Minor and trace elements in early postburial carbonates in deltaic sediments provide information on processes occurring during burial diagenesis. In these sediments, calcite and dolomite record very early events, such as Mg^{2+} incorporation from seawater into calcite and early reduction of seawater SO_4^{2-}. Siderite records later events, such as ongoing Mn reduction and incorporation of Ca, Mg, and trace metals. Incorporation of Ca and Mg is not in proportion to concentrations in porewaters and therefore is complicated by other factors. Trace metals, however, appear to be incorporated into siderite in roughly the proportions in which they occur in the sediment.

References

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