Marine Diagenesis of Shallow Marine Lime-Mud Sediments: Insights from δO^{18} and δC^{13} Data

Abstract. *Shallow marine lime-mud sediments of the Ste. Genevieve Formation (Mississippian), in part of the Illinois Basin, underwent at least three diagenetic changes: (i) local dolomitization in seawater or a brine, producing dolostone having average* δC^{13} *of +2.5 per mille and* δO^{18} *of +1.9 per mille (versus PDB-1); (ii) more usually cementation of unreplaced* $CaCO_3$ *in intrasediment seawater, yielding isotopically marine lime mudstone mainly composed of calcite, 4-micron or finer, with* δO^{18} *of from −1 to +1 per mille; (iii) later partial alteration of* $CaCO_3$ *in permeable dolomitic rocks, by isotopically "lighter" waters, to calcite with an estimated* δO^{18} *of −10 per mille or less. Isotope data appraised by petrographic analysis thus suggest "submarine" cementation of these carbonates in shallow marine conditions.*

Submarine lithification of shallow marine, subtidal, carbonate sediments has been reported recently in "coralgal" reef carbonates (*1*). Most known Recent marine clastic carbonate sediments, however, are unconsolidated down to the post-Pleistocene unconformity. Yet ancient marine limestones, including indurated lime-mud facies, rarely show compaction effects (*2*). This feature led to a suggestion (*2, 3*) that many marine lime-mud carbonates, even in shallow environments, may undergo very early diagenetic "submarine" cementation short distances below the sea floor.

I now report what is apparently the first isotopic evidence of "normal marine" intrasediment cementation of ancient lime-mud sediments under very shallow marine, subtidal conditions. Three different diagenetic events can be distinguished in the particular lime-mud carbonates described here: (i) very early locally distributed dolomitization under marine or near-marine conditions; (ii) early, intrasediment, "submarine" cementation of lime mud; and (iii) a later generation of $CaCO_3$ formed in the presence of formation waters "lighter" in oxygen-18 than was Mississippian seawater.

These interpretations are based on δC^{13} and δO^{18} data for coexisting calcite and dolomite sampled in detail in thin (0.4 to 0.8 m) limestone-to-dolostone transition zones. The recognition of multiple generations of diagenetic calcite required careful petrographic study to apportion "total" calcite δO^{18} among different calcite constituents. Similar coupling of selective isotope analysis and critical petrographic study may reveal that other ancient marine limestones also retain isotopic signs of deposition by seawater or of "submarine" diagenesis, or of both.

The carbonate rocks studied occur in a unit (4 to 7 m thick) of interbedded lime mudstone (*4, 5*) and dolostone in the Ste. Genevieve Formation (Middle Mississippian) in the subsurface of Lawrence County, eastern Illinois; geologically the area is situated in the east-central Illinois Basin. Carbonates that I describe came from stratigraphically equivalent transition zones in three oil wells within an area of about 2.5 km^2 in the Bridgeport oil field. The overall carbonate unit itself is far more widespread, covering at least 400 km^2 and retaining much the same character throughout. Regional evidence suggests that it was deposited as lime mud on a broad, marine, continental shelf of very low relief, and that areas of deposition of lime mud, although probably quite shallow, were rarely if ever awash. There are no signs in these carbonates of emergence or of subaerial (supratidal) sedimentation or diagenesis.

Table 1. Ste. Genevieve Formation: oxygen and carbon isotopic compositions and other properties of carbonate rocks from limestone-to-dolostone transition zones. All δ values are relative to the Chicago PDB-1 standard; their analytical accuracy is discussed (*8*). Abbreviations: Perm, permeability; Dol, dolomite; Carb, carbonate; Cal, calcite; md, millidarcys; D − C, difference between dolomite and calcite.

Sample No.	Porosity (%)	Perm (md)	Dol: Carb (wt %)	δC^{13}‰		δO^{18}‰			ΔO^{18}_{D-C} (‰)
				Dol	Cal	Dol	Cal	"Bulk"	
IG-9	38.6	74.2	100	2.4*		1.8*		1.8	
IG-15	34.3	56.4	100	2.5*		2.8*		2.8	
IG-2	25.3	8.2	79	2.9	0.4	1.8	−7.1	−0.1	8.9
IG-11	13.6	1.2	64	1.7	0.1	3.1	−6.1	− .2	9.2
IG-13	9.0	0.05	51	2.4†	1.0†	1.4†	−4.8†	−1.7	6.2
IG-7	8.1	.05	49	3.0	2.5	2.0	−4.6	−1.3	6.6
IG-12	7.4	.04	31	3.8	2.6†	1.8	−4.1†	−0.9	5.9
IG-14	3.3	.03	18	0.5	0.9	1.3	−4.2	−3.2	5.5
IG-10	3.5	.02	9	1.7†	1.3†	1.2†	−2.5†	−2.2	3.7
IG-1	2.2	.02	6	3.0†	3.2‡	1.6†	−3.3‡	−3.0	4.9

* Arithmetic average of determinations on three different CO_2 preparations from the same sample. † Arithmetic average from two such preparations. ‡ Arithmetic average from four such preparations.

Typical lime mudstone is fairly pure (93 to 99 percent $CaCO_3$), nearly nonporous and impermeable, texturally uniform, "lithographic" limestone, with here and there animal burrows, zones of thin horizontal laminations, and thin fossil-rich zones. Micrite-sized calcite ($\leq 4\ \mu$), in equant polyhedral to loaf-shaped crystals, is by far the main constituent (75 to 85 percent). Other, lesser constituents include microspar calcite 5 to 30 μ in size (5 percent); rare debris of brachiopods, bryozoans, echinoderms, and other marine fossils (2 to 5 percent); dolomite (as much as 5 percent); and clay minerals, detrital quartz, and pyrite (a few percent); with porosity (1 to 3 percent).

Interbedded dolostone is remarkably similar in appearance to the lime mudstone and has many of the sedimentary structures noted above, as well as similar fossils that are present in "negative" as molds. The dolostone is regarded as an early diagenetic replacement of lime-mud facies, but differs from typical lime mudstone in being far more porous and permeable (in Table 1 compare dolostones IG-9 and IG-15 with IG-1, a limestone). Transition zones from limestone to dolostone are marked by striking progressive increases in porosity and permeability.

Samples of Ste. Genevieve carbonates were prepared and analyzed as follows. Core plugs 1.9 cm in diameter, drilled from the cores at vertical intervals of 4 to 8 cm, were subjected to core analysis for total porosity and air permeability. Ends from the samples were thin-sectioned, and the sections were stained with alizarin red-S to accent the calcite. A portion of each sample was crushed finer than 325-mesh ($< 44\ \mu$). Dolomite:calcite ratios of the crushed samples were determined by x-ray diffraction (*6*).

Parcels of CO_2 for isotope analysis were obtained by reaction of portions of crushed samples with 100-percent phosphoric acid at 25°C (*7*) and collection of CO_2 after reaction times of 1 and 72 hours. These two respective parcels of

CO_2 can be attributed largely but not entirely to coexisting calcite and dolomite (*8*). The isotopic compositions of the CO_2 parcels were determined in a 5-cm, 60-deg, sector-type mass spectrometer with a double collecting system and isotope-ratio recording facilities. The isotope results are reported (Table 1) in the standard manner as δO^{18} and δC^{13} relative to the Chicago PDB belemnite standard, and the δO^{18} values for dolomite have been corrected for the phosphoric acid fractionation factor (*9*); reproducibilities were within 0.3 per mille for δO^{18} and 0.1 per mille for δC^{13} with this sample preparation technique.

Isotopic and other properties of the transition-zone carbonate rocks are given in Table 1 and Fig. 1. Isotopically the calcite and dolomite fractions of these rocks are quite different, most notably in δO^{18}. Three features of the data are of particular interest:

1) Dolomite δO^{18} values as a group are nearly constant over the range of dolomite compositions, averaging +1.9 per mille; the least-squares line in Fig. 1 indicates slight enrichment of dolomite in oxygen-18 with increase in dolomite, but a statistical test of the uncertainty of this least-squares line suggests that its slope is very close to zero, so that the trend toward oxygen-18 enrichment may not be real (*8*).

2) Calcites coexisting with dolomites have δO^{18} values that are distinctly "lighter" by 3.7 to 9.2 per mille, and somewhat "lighter" δC^{13} values.

3) Calcites in the more dolomitic (5 to 80 percent), more porous, and more permeable rocks have progressively "lighter" δO^{18} values ranging from about −2 to −7 per mille.

The general uniformity of δO^{18} values for dolomites must mean that the original $O^{18} : O^{16}$ compositions of dolomite either have been shifted uniformly or remain virtually unchanged since dolomitization. The second alternative seems a little more likely in view of the relatively great oxygen-isotope stability of dolomite shown by Epstein *et al.* (*10*), and also in the light of the wide ranges in permeability, bulk chemistry, and calcite δO^{18} now observed in these rocks. If the present dolomite δO^{18} values are indeed close to the original values, dolomitization of Ste. Genevieve lime-mud sediments probably took place in marine, or somewhat hypersaline, intrasediment waters. Ste. Genevieve dolomite δO^{18} values are well within the range (− 0.8 to + 4.9 per mille) and remarkably close to the average (+ 2.1 per mille) reported (*10*) for dolomites from a variety of Recent marine carbonates, and a little higher than δO^{18} values (average, + 0.6 per mille) reported (*11*) for "evaporitic" dolomites in the Mississippian Charles Formation, Saskatchewan.

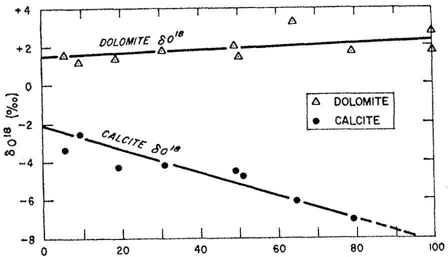

Fig. 1. Oxygen-isotope compositions of calcite and dolomite, versus percentages of dolomite, in transition-zone carbonate rocks of the Ste. Genevieve Formation. The δO^{18} values are relative to PDB-1; the least-squares lines are regression lines of y on x.

Any interpretation of the calcite in these rocks should account for the variations of calcite δO^{18} and δC^{13}, and of $\Delta O^{18}{}_{D-C}$ (Table 1) across transitional zones. But these changes apply to the "total" calcite undifferentiated as to its various constituents: micrite, microspar, and fossils. Point-count analyses of thin sections show that isotopic changes can be accounted for by systematic variations in proportions of micrite and microspar in this "total" calcite fraction. With increase in dolomite, microspar makes up more and more of the unreplaced calcite; micrite, correspondingly less. This increase in proportion of microspar correlates well with the trend toward "lighter" δO^{18} values for "total" calcite (Fig. 2). By extrapolation of the data in Fig. 2, the δO^{18} of "pure" micrite alone is around − 1 to + 1 per mille—not very different from the "total" calcite δO^{18} of lime mudstone sample IG-1 (Table 1). This δO^{18} range may be the norm for undolomitized lime-mudstone facies in the study area. The δO^{18} of microspar alone, more difficult to estimate from Fig. 2, could be anywhere between − 10 and − 15 per mille.

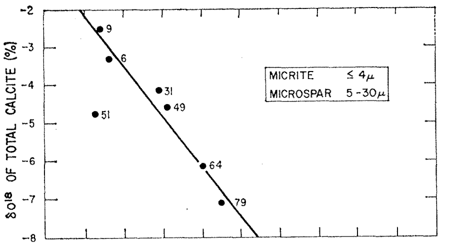

Fig. 2. Oxygen-isotope composition of total calcite versus percentage of microspar in the micrite-plus-microspar fraction of this calcite. Microspar percentages are based on counts totaling 500 per thin section. The numbers beside the points are dolomite percentages (Table 1).

Two interesting implications appear from the calcite data:

1) If the δO^{18} and δC^{13} of Mississippian seawater were like those of present-day seawater, the most micrite-rich lime mudstones in the Ste. Genevieve Formation have marine isotopic compositions; their δO^{18} and δC^{13} are very close to values reported (*8, 12*) for Recent shallow marine lime-mud and other clastic carbonates, and thus differ significantly from the "lighter δO^{18} values reported (*13*) for Mississippian and other Paleozoic marine limestones. Perhaps careful apportionment of "bulk" isotopic composition, among the rock constituents that contribute to the "bulk" values, would show that many "old" marine limestones in fact contain isotopic vestiges of their origins; their marine character has not been wholly erased during diagenesis.

2) Much of the micrite must be marine cement rather than clastic lime mud: carbonate cement of marine origin, most likely precipitated, early in diagenesis, from seawater circulating through intrasediment pores. The idea that cement predominates in the micritic lime mudstones is based on three lines of reasoning advanced by others: (i) lack of compaction features in the lime mudstones implies very early lithification (*2, 3*); (ii) such lithification must have involved the introduction of large volumes of cement (*3, 14*), because Recent lime muds and mixtures of sand and mud have porosities of from 40 to 70 percent (*14*)—far greater than those of the Ste. Genevieve lime mudstones; and (iii) Folk (*5*, p. 35) has shown that micrite crystals contain about 100 times more $CaCO_3$ than do aragonite mud needles of the same maximum "grain size"—another argument for the introduction of carbonate during lithification. If we accept these arguments the isotopic data for Ste. Genevieve mudstone provide new support for the concept, recently shown (*15*), of "submarine" cementation of carbonates. The significant difference is that here we have evidence of cementation of a lime mud, in intrasediment seawater, associated with a shallow marine environment. Analogy with tracts of Recent shallow marine lime-mud suggests that this lithification occurred slightly

(perhaps as deep as a few meters) below the sea floor.

Microspar in transition-zone rocks seems best interpreted as the result of precipitation (further cementation) from isotopically "light" formation waters that must have been depleted in oxygen-18, and perhaps mildly so in carbon-13, relative to Mississippian seawater. The microspar could have originated before dolomitization, in which case its increase in abundance with dolomite content is a net increase resulting from growth of dolomite chiefly at the expense of micrite; the microspar simply "survived" dolomitization better. Alternatively the microspar may postdate the dolomitization, reflecting perhaps more accessibility and "exposure" of unreplaced $CaCO_3$ to formation water in the more porous, permeable, dolomite-rich rocks. The second explanation seems more reasonable since it would not require freshwater diagenesis of $CaCO_3$ prior to marine or hypersaline-water dolomitization, as would the first hypothesis.

If these interpretations are correct, the δO^{18} differences between dolomite and calcite cannot have the same meaning as the 6 to 10 (*10*) or 4 to 7 per mille (*16*) differences estimated for dolomite and calcite coprecipitated at 25°C in isotopic equilibrium; nor can the dolomite be construed as "primary." The following summarized explanation seems more reasonable:

1) The dolomite formed from $CaCO_3$ and has since been quite stable with respect to δO^{18} and δC^{13}. It may have formed (i) solely from $CO_3^=$ provided by $CaCO_3$, without fractionation of $O^{18}:O^{16}$—a dolomitization process that is well supported (*10*); or (ii) in nonequilibrium from marine $CaCO_3$ in intrasediment seawater or derived brine, with oxygen from both the $CaCO_3$ and the water. I favor alternative (ii) because of the micrite interpretations suggested earlier and about to be summarized.

2) Before or after dolomitization (perhaps both) the original unreplaced lime mud became partly cemented by $CaCO_3$ precipitated by intrasediment seawater. The resultant partly lithified but still-permeable lime mudstone consisted mainly of micrite having an estimated δO^{18} between -1 and $+1$ per mille.

3) Unreplaced micrite in the more permeable dolomitic rocks later underwent marked changes in $O^{18}:O^{16}$ and in $C^{13}:C^{12}$ during a long and probably complex sequence of diagenetic events that began in Mississippian time. The net changes in calcite of these rocks were toward depletion in the "heavy" isotopes, probably accomplished by precipitation of $CaCO_3$ from formation waters containing less oxygen-18 and possibly less carbon-13 than seawater contained; the result was microspar.

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17. I thank D. B. MacKenzie, L. C. Pray, L. J. Walters, Jr. (Marathon Oil Company), and S. Epstein (California Institute of Technology) for discussions and criticisms of the manuscript. Epstein and W. S. Ferguson (Marathon Oil Co.) were generous with geochemical guidance, and Walters assisted with statistical evaluation of isotopic data. A. Moore and C. N. Threlkeld did the isotope-ratio analyses, F. C. Capozza did the thin-section point counts, B. J. Wiginton did the x-ray diffraction analyses for calcite and dolomite, and R. B. Mauney did the core analyses. The management of Marathon Oil Co. permitted this publication.

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Argon-40: Excess in Submarine Pillow Basalts from Kilauea Volcano, Hawaii

Abstract. *Submarine pillow basalts from Kilauea Volcano contain excess radiogenic argon-40 and give anomalously high potassium-argon ages. Glassy rims of pillows show a systematic increase in radiogenic argon-40 with depth, and a pillow from a depth of 2590 meters shows a decrease in radiogenic argon-40 inward from the pillow rim. The data indicate that the amount of excess radiogenic argon-40 is a direct function of both hydrostatic pressure and rate of cooling, and that many submarine basalts are not suitable for potassium-argon dating.*

Potassium-argon ages of submarine basalts are now sought for information on the history and development of the ocean basins, especially on possible spreading of the sea floor (*1*). A fundamental assumption made in dating of volcanic rocks is that they contained no radiogenic Ar^{40} at the time they solidified. This assumption is generally true for terrestrial volcanic rocks (*2*) but has not been adequately tested for submarine lava flows.

At some time before solidification, lava flows must lose the radiogenic Ar^{40} that is continually generated by the decay of K^{40}, otherwise the K-Ar clock will not be reset to zero at the time of solidification. This loss of radiogenic Ar^{40} may take place (i) either partly or entirely during the melting leading to magma generation; (ii) while the liquid is rising to the surface or is stored in temporary reservoirs; or (iii) during eruption, as the pressure is released. The time of degassing is uncertain, but the existance of vesicles and lava fountains suggests that some gas is lost during and shortly after eruption. If release of pressure during eruption is important, the hydrostatic pressures at ocean depths may possibly impede loss of argon. Moreover, submarine pillow ba-