

EFFECTS OF SULFATE REDUCTION ON CaCO_3 DISSOLUTION AND PRECIPITATION IN MIXING-ZONE FLUIDS¹

RONALD K. STOESELL

Department of Geology and Geophysics

University of New Orleans

New Orleans, Louisiana 70148

ABSTRACT: Sulfate reduction in the sea-water end member of mixing-zone fluids changes the fluid-saturation indices for carbonate minerals. Mixing-zone fluids were modeled quantitatively using Atlantic sea water and a fresh-water end member from Barbados for sulfate reduction in the presence of goethite, in the absence of goethite, and with back-oxidation of aqueous sulfide to sulfate.

Minor amounts of sulfate reduction enhance dissolution of CaCO_3 in brackish to saline mixing-zone fluids, whereas major amounts of sulfate reduction enhance precipitation in all mixing-zone fluid compositions. Secondary reactions produce either CaCO_3 dissolution or precipitation, which depend in magnitude on the amount of sulfate reduction. Dissolution results from the back-oxidation of aqueous sulfide to sulfate, and precipitation occurs from the transformation of iron oxides to iron sulfides.

pH buffering, due to sulfate reduction, prevents a linear correlation of calcite-saturation indices with the moles of calcite necessary to dissolve or precipitate to reach equilibrium. Without iron sulfide precipitation or the back-oxidation of aqueous sulfide, the moles of calcite that can be dissolved continue to increase up to about 25% sulfate reduction, even though the degree of undersaturation begins to decrease with greater than 5% sulfate reduction. The effects of iron sulfide precipitation and the back-oxidation of aqueous sulfide are greatly enhanced by increasing the amount of sulfate reduction, being generally more than 0.1 g of calcite per kg of water dissolved or precipitated, respectively, at 50% sulfate reduction.

INTRODUCTION

Sulfate reduction in sea water increases alkalinity, resulting in the precipitation of carbonate minerals (Berner 1971). The potential for carbonate precipitation is further increased by the rise in pH due to co-precipitation of iron sulfides during sulfate reduction (Ben-Yaakov 1973). Modeling results of Morse and Mackenzie (1990, their fig. 6-11) indicate that minor amounts of sulfate reduction in sea water can result in carbonate dissolution rather than precipitation, because of the co-production of both H^+ and alkalinity during sulfate reduction. Subsequent back-oxidation of the produced aqueous sulfide to sulfuric acid increases the potential for carbonate mineral dissolution (Smart et al. 1988).

Sulfate reduction should have a significant effect on water-rock interactions in coastal mixing-zone fluids (Nadler et al. 1981). Magaritz and Luzier (1985) reported sulfate reduction in mixing-zone fluids in a coastal dune aquifer in Oregon. Evidence that the bacterially-controlled process occurred in the mixing zone includes sulfate concentration deficiencies, alkalinity excesses, and precipitation of pyrite. Smart et al. (1988) postulated sulfate reduction followed by back-oxidation of gaseous hydrogen sulfide to sulfuric acid in the mixing zone within "blue holes" in the Bahamas to account for the presence of both calcium-carbonate dissolution and iron-sulfide precipitation.

Sulfate reduction is occurring in mixing-zone fluids in coastal limestones along the northeastern coast of the Yucatan Peninsula. Aqueous sulfide concentrations ranging from 2 to 130 ppm were measured in May, 1991 from mixing-zone fluid samples taken in two coastal sinkholes near Xcaret Cave and Tulum (Stoessel et al. 1991). The aqueous sulfide appears to be concentrated in the saline

halocline, being below detection in the fresh water and of lower concentrations in the underlying saline water. Preferential dissolution of aragonite occurred in these limestones in the Pleistocene (Ward and Halley 1985) and is occurring in fractures in the modern mixing zone (Back et al. 1986; Stoessel et al. 1989). Iron sulfides have not been reported in these limestones.

Water-rock reactions in coastal limestones are frequently predicted by mixing an end-member fresh-water composition with the composition of "local" sea water in computer simulations and calculating the resulting saturation indices of carbonate minerals (e.g., Plummer 1975; Back et al. 1986; Stoessel et al. 1989). However, the sea-water end member may have a reduced sulfate composition when it mixes inland with fresh water. As sea water moves landward, under the fresh-water wedge, sulfate reduction may remove much of the sulfate, replacing it with hydrogen ions, hydrogen sulfide, and bicarbonate. Subsequent mixing with fresh water will produce saturation indices that differ greatly from those computed using sea water with normal sulfate composition. Similar effects will be produced by sulfate reduction occurring after mixing. The saturation indices will be further changed by the presence of iron oxides which reduce hydrogen ion concentrations through precipitation of iron sulfides or by the oxidation of aqueous sulfide which increases hydrogen ion concentrations.

Quantitative predictions of the effects of sulfate reduction in mixing-zone fluids within coastal limestones are presented in this study. The pathways modeled in this study are shown in Figure 1 with their qualitative effects on CaCO_3 precipitation and dissolution. These pathways assume that sulfate reduction has occurred in the *presence* of iron oxides *without* aerobic oxidation of aqueous sulfide, in the *absence* of iron oxides *without* aerobic oxidation of aqueous sulfide, and in the *absence* of iron oxides *with* aerobic oxidation of aqueous sulfide.

Under earth surface conditions, reaction kinetics can

¹ Manuscript received 5 March 1991; accepted 12 September 1991.

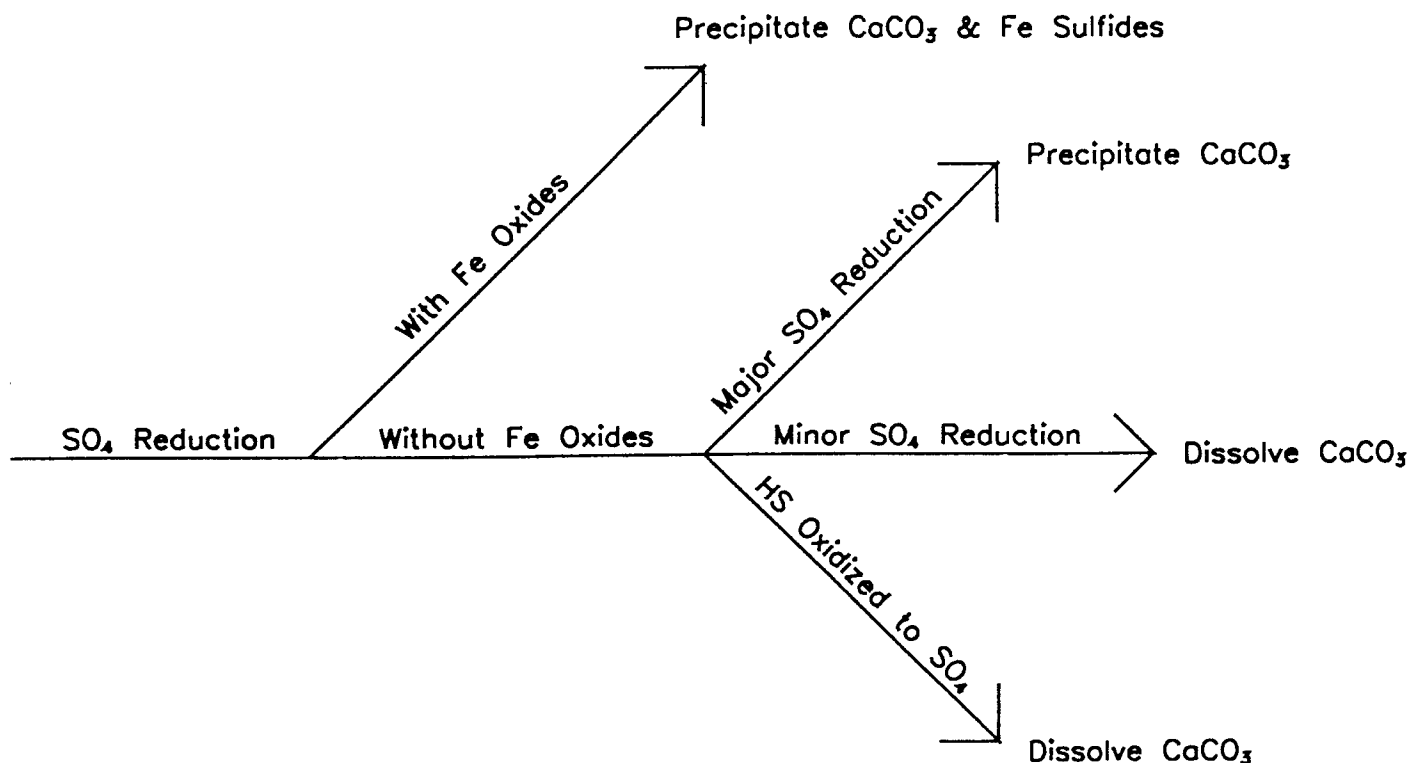


FIG. 1.—Schematic drawing showing pathways modeled in this study for sulfate-reduced mixing-zone fluids and the resulting qualitative effects on calcite dissolution in the mixing zone.

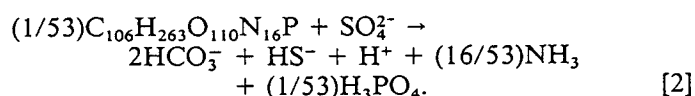
control the extent of sulfate reduction, aerobic oxidation, and the reactivity of minerals with aqueous solutions, such as the transformation of goethite to pyrite in the presence of aqueous sulfide. Reaction kinetics are beyond the scope of this modeling study, which utilizes equilibrium thermodynamics to describe aqueous speciation and to set limits on mineral dissolution and precipitation. Sulfate reduction in the aqueous solutions was assumed to have occurred prior to fluid–mineral reactions through the oxidation of carbohydrates. This reduction implies that sufficient organic matter was present in contact with anoxic waters for bacteria to reduce the aqueous sulfate. When aerobic oxidation of the produced aqueous sulfide was assumed to occur, all of the available aqueous sulfide was assumed to have been oxidized. This oxidation implies that the aqueous solution had come into contact with sufficient amounts of dissolved oxygen for the oxidation to occur. Aerobic oxidation of solid sulfides was not considered; however, dissolution and oxidation of solid sulfides would have a similar effect as oxidation of aqueous sulfide.

The overall anaerobic aqueous sulfate reaction of carbohydrates, presumably controlled by bacteria (genus *Desulfovibrio*), can be simply written as (Berner 1971)



The Redfield composition of organic matter includes nitrogen and phosphorus and is commonly used to describe sulfate reduction during organic diagenesis (Froelich et al. 1979; Morse and Mackenzie 1990, p. 268). Sulfate

reduction, utilizing the Redfield composition, can be written as

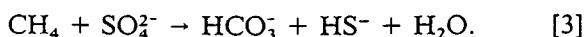


The bicarbonate and hydrogen ion production in reaction 2 is the same as in reaction 1; however, the pH will be affected by the buffering of ammonia and phosphoric acid. The ammonia produced during sulfate reduction will raise the pH by combining with hydrogen ions to form ammonium, raising the aqueous saturation state with respect to CaCO_3 . In this study, the production of *minor* amounts of ammonia and *trace* amounts of phosphoric acid have been neglected.

Organic matter oxidation by reduction of iron and manganese oxides, without the precipitation of metallic sulfides, will also raise the pH and increase bicarbonate concentrations, promoting the precipitation of CaCO_3 (Froelich et al. 1979). However, the *trace* iron and manganese concentrations in ground waters (e.g., in Table 2) indicate that iron and manganese reduction is accompanied by precipitation processes. One of the pathways modeled in this study includes the reduction of ferric iron in goethite to form iron sulfides. A similar pathway for manganese was not modeled; however, the effects on CaCO_3 saturation are similar.

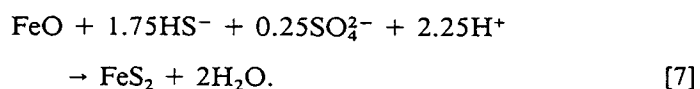
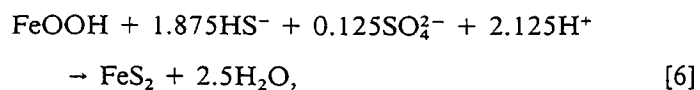
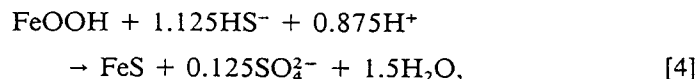
The carbon and hydrogen stoichiometry of the organic matter controls the production of hydrogen and bicarbonate ions, affecting the saturation state of CaCO_3 . In

reaction 3 below, methane oxidation results in half the production of bicarbonate ions, relative to reaction 1, and no hydrogen ions. Reaction 3 will promote precipitation of CaCO_3 , whereas, as discussed below, reaction 1 can produce either dissolution or precipitation of CaCO_3 .



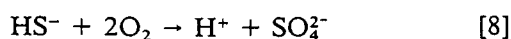
Following the lead of previous researchers (e.g., Berner 1971; Stumm and Morgan 1981; Morse and Mackenzie 1990), the simple carbohydrate stoichiometry has been assumed to be representative of the organic matter, and reaction 1 was used to describe sulfate reduction. Reaction 1 tends to promote carbonate dissolution through the release of hydrogen ions; however, excessive buildup of bicarbonate ions in solution will result in precipitation of carbonate minerals. The former effect predominates with minor amounts of sulfate reduction (Morse and Mackenzie 1990, their fig. 6-11), and the latter effect predominates with major amounts of sulfate reduction (Berner 1971).

The effect of the precipitation of iron sulfides during sulfate reduction is to raise the pH (Ben-Yaakov 1973). The destruction of hydrogen ions can be represented schematically by the transformation of goethite and FeO to amorphous FeS and pyrite in the following aqueous reactions:



The reactions were written to conserve iron in the solid phases, reflecting the trace concentrations of aqueous iron in natural waters. The overall change in pH, when combined with reaction 1, is to generally raise the pH, shifting the solution compositions towards carbonate supersaturation, eliminating any enhancement of carbonate dissolution through sulfate reduction.

The effects of sulfate reduction can be modified by the production of hydrogen ions through the back-oxidation of aqueous sulfide to sulfuric acid. Such oxidation will not occur in the reduced environment of sulfate reduction but may occur if waters become oxygenated as they move through fractures opening to the atmosphere or mix with oxygenated water. The lowering of the pH, indicated in the sulfide-oxidation reaction below, will produce carbonate-mineral dissolution.



Calcite-saturation indices were computed for compo-

TABLE 1.—Sea-water and fresh-water end members in ppm#

	Sea Water-Bottom Bay	Fresh Water-Three Houses Sp.
Cl	18,754	62
SO ₄	2720	25
HCO ₃	132	253
NO ₃	b.d.	33.1
PO ₄	b.d.	b.d.
SiO ₂	0.15	14.5
Ca	388	87.2
Mg	1249	10.4
K	380	2.06
Na	10,467	44.5
Sr	6.67	0.94
Fe	0.15*	0.25
Mn	0.02*	<0.01
TDS	34,100	530
Charge Balance ± meq/kg H ₂ O	-0.56	+0.29
pH	8.00	7.10
T°C	29.3	27.0

Analytical data are from samples collected and analyzed by Stoessell in June, 1989. The data are in ppm unless otherwise noted.

* Fe and Mn values are estimates in sea water because atomic absorption measurements were affected by the sea-water matrix.

sitions from mixing the sulfate-deficient sea water with fresh water in the presence and absence of goethite. For those solutions lacking goethite, saturation indices were also computed for compositions in which the produced aqueous sulfide was completely oxidized to sulfate. For all these solutions the moles of calcite were then computed that needed to be dissolved or precipitated to bring the fluids to calcite equilibrium.

The general effects of sulfate reduction on aragonite dissolution and precipitation in mixing-zone fluids are identical to those for calcite. Aragonite metastability relative to calcite results in aragonite saturation indices being shifted slightly in the direction of undersaturation. More aragonite can be dissolved in regions of initial fluid undersaturation, and less aragonite can be precipitated in regions of initial fluid supersaturation.

METHODOLOGY

The fresh-water end member used in the study was sampled in June, 1989 from the Three Houses Spring in a late Pleistocene limestone near the eastern coast of Barbados, and the sea-water end member was taken from the adjacent Atlantic Ocean at Bottom Bay. Due to limestone dissolution, ground water from the Three Houses Spring was at near equilibrium with respect to calcite, having a pH of 7.1 and calcium and bicarbonate concentrations of 90 and 250 ppm, respectively. The spring was also sampled at the end of the rainy season in November, 1989. The pH was 7.0, and calcium and bicarbonate concentrations had decreased to 80 and 230 ppm, respectively. The fluid compositions of the end members are listed in Table 1. Sulfide compositions were not measured in the field for these fluids, and it is not evident from petrology studies of the Pleistocene limestones (Humphrey 1988, and personal communication 1990) if sulfate

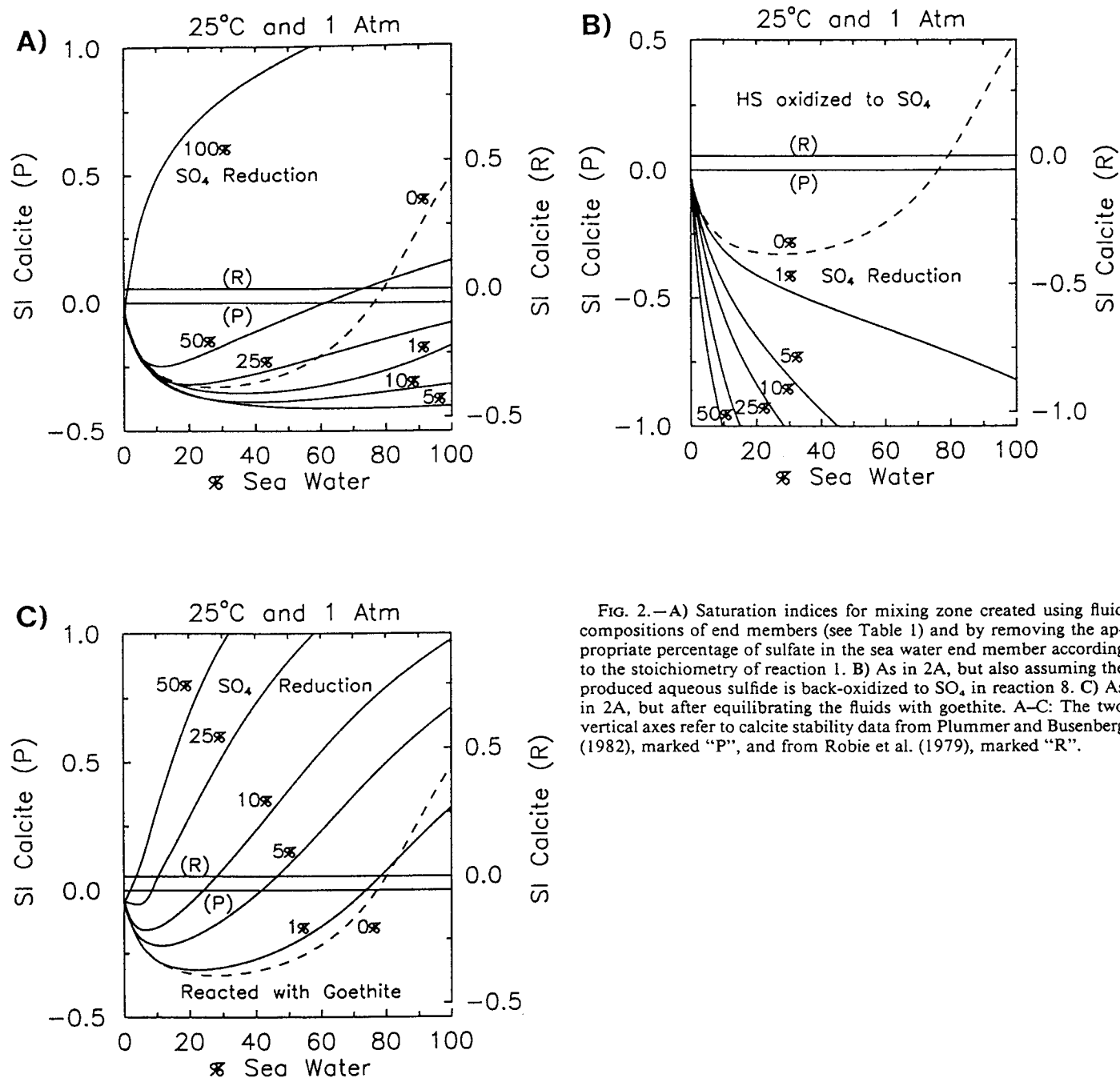


FIG. 2.—A) Saturation indices for mixing zone created using fluid compositions of end members (see Table 1) and by removing the appropriate percentage of sulfate in the sea water end member according to the stoichiometry of reaction 1. B) As in 2A, but also assuming the produced aqueous sulfide is back-oxidized to SO_4 in reaction 8. C) As in 2A, but after equilibrating the fluids with goethite. A–C: The two vertical axes refer to calcite stability data from Plummer and Busenberg (1982), marked “P”, and from Robie et al. (1979), marked “R”.

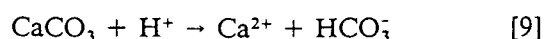
reduction is actually occurring in the Barbados coastal mixing zone. The modern mixing zone along this coast is the subject of ongoing studies of Quaternary dolomites and carbonate dissolution (Kimbell et al. 1990).

The end-member fluids were used as an example of a “typical” mixing zone in which the crossover point from calcite undersaturation to supersaturation occurs at about 75% sea-water composition in the absence of sulfate reduction. The bulk fluid chemistry of the sea-water end member was then modified by sulfate reduction, using the stoichiometry of reaction 1. The percentage of sulfate reduction corresponded to the percentage of initial sulfate in the sea-water end member that was reduced. For the

pathway involving back-oxidation of aqueous sulfide, the bulk chemistry of the sea-water end member was further modified using the stoichiometry of reaction 8. During subsequent modeling, the chemical differences along the various pathways result from aqueous species distributions calculated from equilibrium thermodynamics as a result of different fluid–mineral reactions carried out to thermodynamic equilibrium.

The Fortran computer program REACT, described in Stoessel (1988) and Stoessel et al. (1989), was used on a Zenith personal computer model 386 to compute the saturation indices and the moles of calcite needed to reach equilibrium. For calcite, the saturation index, SI, is de-

finer for the dissolution reaction:



as

$$\text{SI} = \log (a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-} / a_{\text{H}^+}) - \log K \quad [10]$$

where K is the reaction equilibrium constant and a_i is the activity of the i th aqueous species. Because of solution equilibrium between HCO_3^- and CO_3^{2-} , an identical SI will be computed for calcite if the reaction is written to CO_3^{2-} . The calcite-saturation values in Figure 2 are referenced to two different vertical axes, marked "P" and "R", respectively, using calcite stability data from Plummer and Busenberg (1982) and from Robie et al. (1979). The difference between the two axes, 0.055 SI units, represents the uncertainty in SI values because of uncertainty in calcite stability. For a discussion of general uncertainties due to errors in measured solution compositions and computation of aqueous activities, the reader is referred to Merino (1979). The standard-state mineral data in REACT, used to react goethite to equilibrium (shown in Fig. 2C) came from Robie et al. (1979) and to react calcite to equilibrium (shown in Fig. 3) came from Plummer and Busenberg (1982). The iron sulfides considered in modeling were pyrite and pyrrhotite, of which pyrite was more stable. Their standard-state data were from the Berkeley Data Bank (H. Helgeson, personal communication 1989).

RESULTS AND DISCUSSION

Saturation Indices

The SI values for calcite are plotted versus percent sea water for several conservative mixing curves in Figure 2A, B and C. The dashed mixing curve indicating 0% sulfate reduction is the baseline curve for comparison purposes. This mixing curve crosses the "Plummer" equilibrium line from undersaturation to supersaturation at about 75% sea water.

Sulfate reduction in the absence of secondary reactions (e.g., the back-oxidation of aqueous sulfide to sulfate or the precipitation of iron sulfides) is shown in the conservative mixing curves in Figure 2A. For up to 5% sulfate reduction, the mixing curves are shifted increasingly towards undersaturation, to the extent that undersaturation occurs throughout the entire range of percent sea-water compositions. With greater sulfate reduction, the curves move back towards supersaturation, creating a situation in which dissolution can only take place in the fresh-water portion (< 50% sea water composition) with greater than 50% sulfate reduction. Eventually, as the amount of sulfate reduction approaches 100%, only calcite precipitation can occur due to mixing. These trends can be related to reaction 1 in which the lowering of pH causes undersaturation with minor amounts of sulfate reduction and the increase in bicarbonate causes supersaturation with major amounts of sulfate reduction.

The mixing curves in Figure 2B have been computed assuming complete oxidation of the produced aqueous sulfide to sulfate. The curves are shifted towards increased

undersaturation of calcite, relative to the dashed baseline curve. The oxidation of sulfide produces undersaturation through the formation of sulfuric acid in reaction 8.

Smart et al. (1988) have reported iron sulfides in carbonate rock undergoing dissolution in sinkholes in the modern mixing zone on South Andros Island in the Bahamas. These authors attributed the sulfides to sulfate reduction controlled by bacteria. Subsequent precipitation of iron sulfides due to reaction between iron oxides and H_2S would be expected in an anaerobic environment (Morse et al. 1987). The mixing curves shown in Figure 2C have been recalculated from those shown in Figure 2A by reacting the solutions to equilibrium with goethite. The effect is to shift the SI values towards supersaturation through the precipitation of iron sulfides. This trend relates directly to the rise in pH in reactions 4–7 produced by the transformation of iron oxides to iron sulfides. Interestingly, Smart et al. (1988) report enhanced dissolution in this region and not precipitation. They suggest that some of the dissolution is related to sulfuric acid (reaction 8, Fig. 2B) produced by oxidation of gaseous hydrogen sulfide rising through the sinkholes into oxygenated waters. This reaction is not expected to be important in porous, non-fractured limestone, but it may commonly occur in fracture-dominated systems which have large vertical conduits such as sinkholes.

Moles of Calcite Dissolved or Precipitated

The moles of calcite needed to dissolve or precipitate to reach equilibrium are shown in Figure 3A for solutions in which sulfate reduction has occurred without secondary reactions (i.e., no back-oxidation of aqueous sulfide or precipitation of iron sulfides), in Figure 3B for solutions in which back-oxidation of all aqueous sulfide to sulfuric acid has occurred, and in Figure 3C for solutions equilibrated with goethite. Positive moles in Figure 3 indicate precipitation, and negative moles indicate dissolution. The initial SI indices, prior to calcite reaction, for Figure 3 are given in Figure 2: 2A corresponds to 3A, etc. As in Figure 2, the dashed curves on Figure 3 correspond to the baseline condition of no sulfate reduction. The baseline curves indicate that both dissolution and precipitation, as a function of percent sea water, occur in the absence of sulfate reduction.

The largest amounts of predicted calcite dissolution shown in Figure 3B are due to the formation of sulfuric acid from the oxidation of aqueous sulfide. These amounts reach 0.1 g/kg H_2O in saline mixing-zone fluids at 5% sulfate reduction and continue to increase with greater sulfate reduction.

For any given percent sea-water composition, without oxidation of aqueous sulfide and with the goethite transformation to iron sulfides in reactions 4 and 6, calcite dissolution is always less or precipitation is always more than without sulfate reduction (Fig. 3C). These trends shift systematically in the direction of more calcite precipitation with increasing amounts of sulfate reduction, reaching 0.1 g/kg H_2O in saline mixing-zone fluids at 25% sulfate reduction. Precipitation of iron sulfides signifi-

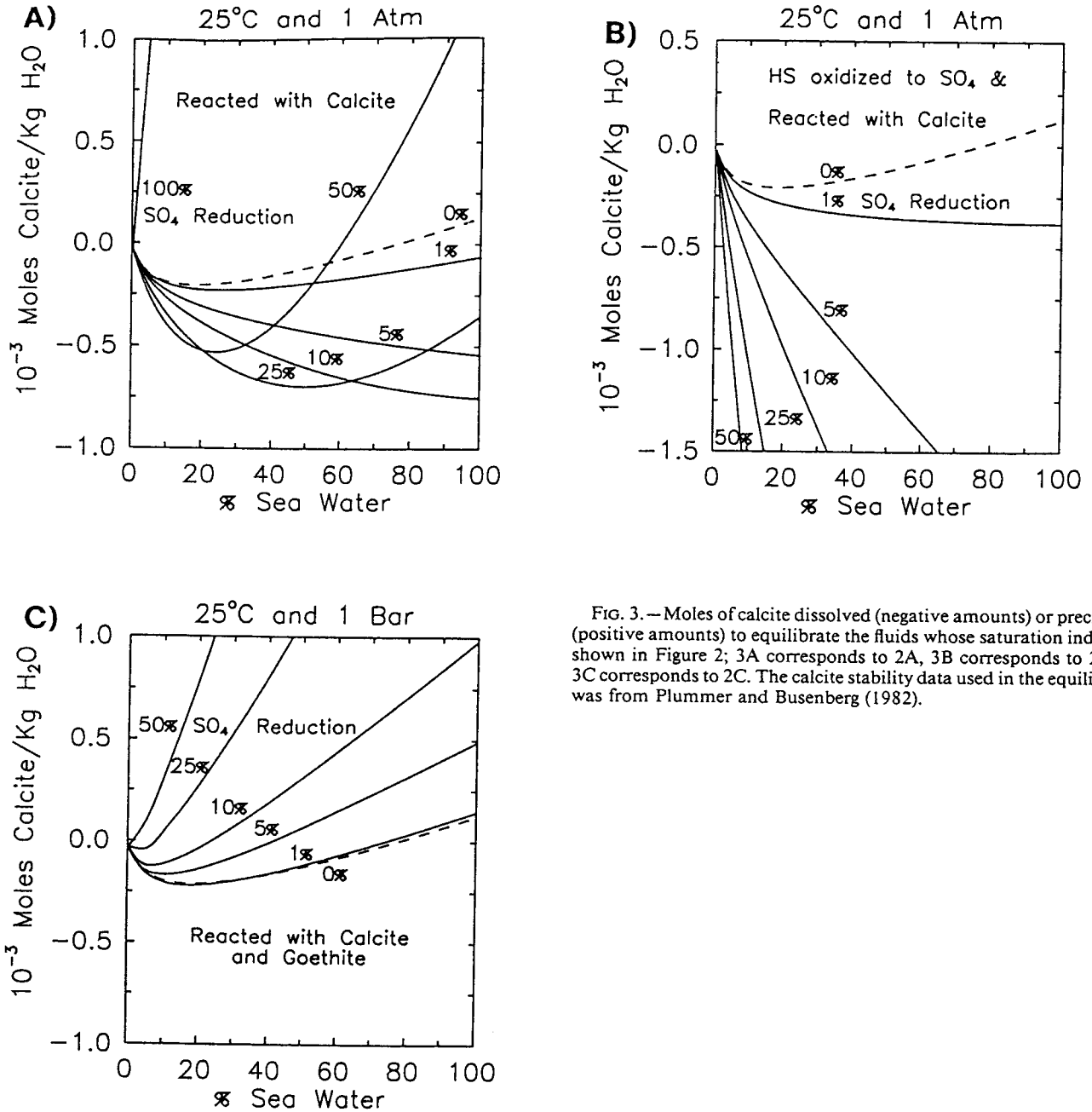


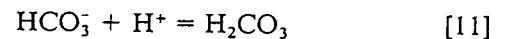
FIG. 3.—Moles of calcite dissolved (negative amounts) or precipitated (positive amounts) to equilibrate the fluids whose saturation indices are shown in Figure 2; 3A corresponds to 2A, 3B corresponds to 2B, and 3C corresponds to 2C. The calcite stability data used in the equilibration was from Plummer and Busenberg (1982).

cantly increases the potential for carbonate-mineral precipitation in mixing-zone fluids.

The situation is more complex for pathways involving sulfate reduction without reaction with goethite (i.e., without precipitation of iron sulfides) and without oxidation of aqueous sulfide to sulfate. The saturation indices in Figure 2A shift towards undersaturation as the amount of sulfate reduction rises to about 5%, and then they shift back towards saturation with increasing sulfate reduction. However, the moles of calcite needed to be dissolved to reach equilibrium in Figure 3A still generally increase even though the saturation indices indicate less undersaturation. This trend continues until the amount of sulfate reduction increases to about 25%, before reversing

towards decreasing amounts of calcite dissolution and/or increasing amounts of precipitation.

The trends described above can be explained by the pH buffering effect of carbonic acid and bicarbonate (Ben-Yaakov 1973). Sulfate reduction in reaction 1 produces both hydrogen and bicarbonate ions in a 1:2 ratio, representing an increase in carbonate alkalinity. Formation of carbonic acid (actually dissolved CO₂ and water) in reaction 11 buffers the H⁺ concentrations:



preventing the calcite SI in reaction 9 from continuously decreasing with increasing amounts of sulfate reduction. Eventually the increase in HCO₃⁻ concentrations causes

the calcite SI to rise above that representing the baseline condition of no sulfate reduction. This occurs even though the pH is lowest in the solutions with the most sulfate reduction.

Fluids that have undergone large amounts of sulfate reduction are strongly pH buffered, requiring substantial amounts of CaCO_3 dissolution and precipitation to reach equilibrium. The pH is locked into a narrow range because of the large buffering effect of reaction 11 in the presence of high concentrations of bicarbonate. The result is that calcium and bicarbonate concentrations, already high in the solution, have to change significantly to reach equilibrium. For these changes to occur, an increased amount of dissolution or precipitation must take place. These amounts are generally greater than in the baseline environment, where changing the pH is the principal path to reach equilibrium. The significance of this point can be shown by comparing Figures 2A and 3A. For undersaturated solutions, the calcite SI can be lower in the baseline environment than for moderate amounts of sulfate reduction. For example, in Figure 2A the SI at the 50% sea-water point on the 0% curve lies below the same point on the 25% curve, implying that more calcite dissolution could occur for 0% sulfate reduction. However, from Figure 3A at 50% sea water, approximately five times more calcite can be dissolved at 25% sulfate reduction than at 0% sulfate reduction.

Chemical Indications of Sulfate Reduction

An obvious indication of aqueous sulfate reduction is the presence of authigenic iron sulfides in the rock (reactions 4–7). Correspondingly, the presence of unaltered iron oxide minerals implies a lack of sulfate reduction.

A deficiency of aqueous sulfate (reaction 1), relative to that expected by conservative mixing, could be interpreted as due to sulfate reduction. This deficiency could be masked by gypsum dissolution and/or reoxidation of sulfide in oxygenated waters. Unfortunately, aqueous sulfate concentration measurements (commonly made by precipitation as non-radioactive barium sulfate) are often not very accurate and 5 to 10% errors can often be expected in these measurements, camouflaging minor amounts of sulfate reduction.

Hydrogen sulfide concentrations in the ppm level should indicate sulfate reduction (reaction 1). Hydrogen sulfide will oxidize in the field, necessitating measurements soon after collection. Field detection methods (by iodine titrimetric procedures) are only accurate to about 0.5 ppm, causing problems measuring trace concentrations. However, trace amounts can easily be detected by the odor of degassing hydrogen sulfide. Absence of hydrogen sulfide may be due to removal by precipitation of iron sulfides or by oxidation in oxygenated waters.

Probably the most accurate indicator of sulfate reduction would be from the excess carbonate alkalinity contributed by reaction 1. Excess carbonate alkalinity is the increase in carbonate alkalinity above that expected from conservative mixing plus additions and subtractions due to carbonate-mineral dissolution and precipitation (e.g.,

reaction 9). These additions and subtractions have to be estimated from differences in calcium and magnesium concentrations from those expected from conservative mixing and gypsum dissolution. The excess carbonate alkalinity is easily computed from the measured alkalinity in the absence of gypsum dissolution and reactions affecting the overall alkalinity such as the precipitation of iron sulfides (reactions 4–7) and the oxidation of solid and/or aqueous sulfides (reaction 8).

Calcite saturation indices that are both undersaturated and below those predicted by conservative mixing could be a good indication of sulfate reduction. This is because both minor sulfate reduction (in the absence of iron sulfide precipitation) and oxidation of hydrogen sulfide will shift calcite-saturation indices below the conservative-mixing curve. Sulfate reduction could be obscured if calcite dissolution and carbon dioxide degassing occur, because both of these processes can shift undersaturated waters above the conservative-mixing curve.

CONCLUSIONS

- 1) In modeling carbonate-mineral SI values in ground water within coastal mixing zones, the saline end member should not be oceanic sea water but saline ground water corresponding to that present below the brackish-water lens.
- 2) Sulfate reduction followed by the oxidation of aqueous sulfide in oxygenated waters promotes carbonate mineral dissolution.
- 3) Sulfate reduction combined with the precipitation of iron sulfides promotes less carbonate-mineral dissolution and more carbonate-mineral precipitation.
- 4) A moderate amount of sulfate reduction, up to 40% for some salinities, will enhance carbonate-mineral dissolution in the absence of the precipitation of iron sulfides. This enhancement can significantly increase (by a factor of 5) the amount of carbonate dissolution expected with non-sulfate-reduced fluids. Increasing the amount of sulfate reduction above 40% promotes less carbonate mineral dissolution or (if supersaturated) more carbonate mineral precipitation, relative to non-sulfate-reduced fluids.
- 5) The presence of iron sulfides in coastal limestones indicates that sulfate reduction took place, whereas, the absence of iron sulfides in coastal limestone combined with the presence of iron oxides implies an absence of sulfate reduction. In ground waters within coastal limestones, sulfide concentrations, sulfate concentrations, and carbonate alkalinites can be used as indicators of sulfate reduction after appropriate corrections are made for contributions due to conservative mixing, carbonate-mineral dissolution and/or precipitation, and assuming an absence of gypsum dissolution and reoxidation of aqueous sulfide. Calcite-saturation indices which are both undersaturated and below those predicted by conservative mixing can be a sensitive indicator of minor amounts of sulfate reduction and/or major amounts of sulfate reduction in

which the aqueous sulfide has been back-oxidized to sulfate.

ACKNOWLEDGMENTS

W.C. Ward suggested investigating sulfate reduction in mixing-zone fluids, and Y.H. Moore edited the manuscript. B. Ward and J.D. Humphrey made contributions on this topic, and C.H. Moore reviewed an early manuscript version. Exxon Production Research Company supplied field support in Barbados for sampling the fluid end members. The manuscript benefitted from reviews by P. Baker, the associate editor, and two journal reviewers: E. Burton and G. Tribble.

REFERENCES

- BACK, W., HANSHAW, B.B., HERMAN, J.S., AND VAN DRIEL, J.N., 1986, Differential dissolution of a Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico: *Geology*, v. 14, p. 137-140.
- BEN-YAAKOV, S., 1973, pH buffering of pore water of recent anoxic marine sediments: *Limnology Oceanography*, v. 18, p. 86-94.
- BERNER, R.A., 1971, *Principles of Chemical Sedimentology*: New York, McGraw-Hill, 240 p.
- FROELICH, P.N., KLINKHAMMER, G.P., BENDER, M.L., LUEDTKE, N.A., HEATH, G.R., CULLEN, D., DAUPHIN, P., HAMMOND, D., HARTMAN, B., AND MAYNAMRD, V., 1979, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis: *Geochimica et Cosmochimica Acta*, v. 43, p. 1075-1090.
- HUMPHREY, J.D., 1988, Late Pleistocene mixing zone dolomitization, southeastern Barbados, West Indies: *Sedimentology*, v. 35, p. 327-348.
- KIMBELL, T.N., HUMPHREY, J.D., AND STOESSELL, R.K., 1990, Quaternary mixing zone dolomite in a cored borehole, southeastern Barbados, West Indies (abstract): *Geological Society of America, Abstracts with Programs*, v. 22, p. 179.
- MAGARITZ, M. AND LUZIER, J.E., 1985, Water-rock interactions and seawater-freshwater mixing effects in the coastal dunes aquifer, Coos Bay, Oregon: *Geochimica et Cosmochimica Acta*, v. 49, p. 2515-2525.
- MERINO, E., 1979, Internal consistency of a water analysis and uncertainty of the calculated distribution of aqueous species at 25°C: *Geochimica et Cosmochimica Acta*, v. 43, p. 1533-1542.
- MORSE, J.W. AND MACKENZIE, F.T., 1990, *Geochemistry of Sedimentary Carbonates*: New York, Elsevier, 707 p.
- MORSE, J.W., MILLERO, F.J., CORNWELL, J.C., AND RICHARD, D., 1987, The chemistry of hydrogen sulfide and iron sulfide systems in natural waters: *Earth Science Reviews*, v. 24, p. 1-42.
- NADLER, A., MAGARITZ, M., AND MAZAR, E., 1981, Chemical reactions of seawater with rocks and freshwater: experimental and field observations on brackish waters in Israel: *Geochimica et Cosmochimica Acta*, v. 44, p. 879-886.
- PLUMMER, L.N., 1975, Mixing of sea water with calcium carbonate ground water, in Whitten, E.H.T., ed., *Quantitative Studies in Geological Sciences*, Geological Society of America Memoir 142, p. 219-236.
- PLUMMER, L.N. AND BUSENBERG, E., 1982, The solubilities of calcite, aragonite, and vaterite in CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O: *Geochimica et Cosmochimica Acta*, v. 46, p. 1011-1040.
- ROBIE, R.A., HEMINGWAY, B.S., AND FISHER, J.R., 1979, Thermodynamic properties of minerals and related substances at 298.15°K and 1 bar pressure and at higher temperatures: U.S. Geological Survey Bulletin 1452, 456 p.
- SMART, P.L., DAWANS, J.M., AND WHITAKER, F., 1988, Carbonate dissolution in a modern mixing zone: *Nature*, v. 335, p. 811-813.
- STOESSELL, R.K., 1988, 25°C and 1 atm dissolution experiments of sepiolite and kerolite: *Geochimica et Cosmochimica Acta*, v. 52, p. 365-374.
- STOESSELL, R.K., WARD, W.C., FORD, B.H., AND SCHUFFERT, J.C., 1989, Water chemistry and CaCO₃ dissolution in the saline part of an open-flow mixing zone, coastal Yucatan Peninsula, Mexico: *Geological Society of America Bulletin*, v. 101, p. 159-169.
- STOESSELL, R.K., MOORE, Y.H., AND J.G. COKE, 1991, Hydrogen sulfide in mixing-zone fluids, northeastern coastal Yucatan Peninsula, Mexico (abstract): *Geological Society of America, Abstracts with Programs*, v. 23, p. 382.
- STUMM, W. AND MORGAN, J.J., 1981, *Aquatic Chemistry*: New York, Wiley-Interscience, 780 p.
- WARD, W.C. AND HALLEY, R.B., 1985, Dolomitization in a mixing zone of near seawater composition, late Pleistocene, northeastern Yucatan Peninsula: *Journal of Sedimentary Petrology*, v. 55, p. 407-420.