Geochemistry and isotope systematics of sulphur in the mixing zone of Bahamian blue holes

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Abstract—A profile of aqueous S species concentrations and stable isotope compositions is presented for the mixing zone of Cousteau's Blue Hole, North Andros, Bahamas, together with similar, but less detailed results from two other blue holes. These data show that S^0 and S^{2-} are produced by bacterially mediated sulphate reduction near the base of the mixing zone and that these species are reoxidized at shallower levels. Acidity generated by oxidation can contribute to corrosion of limestone wall-rock. Estimated rates of such corrosion range up to 1200 mm wall-rock recession per 10 ka at Cousteau's Blue Hole (equivalent to 16% porosity generation per 10 ka) and are comparable with rates of dissolution caused by inorganic mixing corrosion.

INTRODUCTION

BLUE holes are natural, water-filled caverns developed in the Bahamas carbonate platform. Those exposed on the islands contain a freshwater lens at their surface but pass through a stratified mixing zone to saline water at depth. These blue holes can be explored by the use of specialized cave-diving techniques (PALMER, 1985) and therefore provide a relatively accessible route by which the mixing zone may be sampled and chemical processes acting here may be studied. Analogous processes may be acting throughout the mixing zone in the aquifer, hence studies in blue holes can provide a valuable window into the hydrogeochemistry of the freshwater–saline interface in the aquifer as a whole.

Pore-water undersaturation with respect to calcite and aragonite can be generated by mixing of fresh and saline groundwaters (BOGLI, 1964; PLUMMER, 1975; WIGLEY and PLUMMER, 1976) and may be responsible for the development of porosity in mixing zones within carbonate aquifers (HANSHAW and BACK, 1980; SANFORD and KONIKOW, 1989). However, SMART *et al.* (1988) proposed that bacterially mediated processes may further enhance undersaturation (and consequently increase corrosion) in the mixing zones of Bahamian blue holes. Here, we report the results of a chemical and isotopic investigation of the systematics of S species in the water

column of blue holes and assess the role of acidity generated by bacterially mediated S redox reactions in corroding the limestone wall-rocks.

Karstic and mixing zone corrosion of carbonate rocks provides secondary porosity important in the formation of many oil reservoirs. Mixing zone porosity in carbonate rocks is characterized by an essentially horizontal zone of well connected matrix and cave porosity which ideally rims the flanks of topographic highs. Such features can be recognized in seismic sections (e.g. WIGLEY *et al.*, 1988) and form important components of porosity in many carbonate oil reservoirs, e.g. North Bridgeport Field, Illinois (CHOQUETTE and STEINMAN, 1985); San Andres Formation (CRAIG, 1988); Amposta Marino Field (WIGLEY *et al.*, 1988). In this study we document the occurrence of a bacterially mediated process which may significantly enhance rates of formation of mixing zone porosity and which should be considered in the evaluation of porosity development in ancient carbonate rocks with reservoir potential.

SAMPLING AND ANALYTICAL PROCEDURES

Sampling

Water samples were collected at four blue holes on North Andros (Fig. 1). A complete profile of water samples was taken through the mixing zone in Cousteau's Blue Hole and
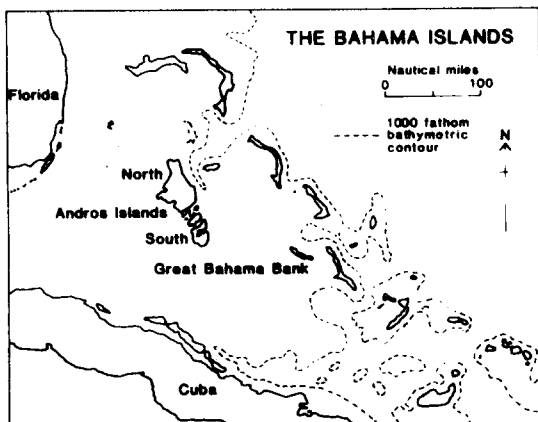
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FIG. 1. Location map for Andros Islands, Bahamas.

The SO_2 gases were analyzed on a VG Isogas SIRA 10 gas source mass spectrometer and the data were corrected using standard procedures (e.g. COLEMAN, 1980). Sulphur isotopic compositions are reported in standard delta notation relative to the Canon Diablo Troilite (CDT) standard. Internal standards were: for sulphides a chalcopyrite standard, British geological Survey CP-1 ($-4.56‰$ CDT); for SO_4 a sea water sulphate standard ($+20.2‰$ CDT, calibrated against International Atomic Energy Authority (IAEA) OGS-1). Analyses of IAEA NZ-1 gave $0.23 \pm 0.16‰$ (2σ). The small masses of material recovered for analysis prevented duplicate analysis of most samples. However, at depth 28 m in Cousteau's Blue Hole duplicate water samples were taken and a duplicate isotopic analysis performed on the SO_4^{2-} recovered from one of them; all three sulphate–sulphur isotopic analysis fall within a range of $0.4‰$.

RESULTS

Chemical profile

The variation of conductivity, SO_4^{2-} and sulphide concentrations with depth in Cousteau's Blue Hole are given in Fig. 2. The mixing zone is characterized by a marked colour zonation (Fig. 2); below the clear freshwater lens the mixing zone is hazy and has a distinct brown layer near its base forming the inter-

additional samples were taken from No. 10 and Ken's Blue Holes for comparison. Undisturbed water samples were collected by diving and filling 2l plastic tubes which were sealed underwater. Conductivity and temperature of the water were measured *in situ* and were used to target sample depths. On site, the samples were filtered through 0.45 μm membrane filters and the particulate material, including any colloidal S, dried and retained for analysis. Sulphide in the filtrate was then precipitated with zinc acetate and retained after a second filtering for isotopic analysis. Finally, SO_4^{2-} was precipitated with barium chloride. Further aliquots were: (1) acidified for later analysis of SO_4^{2-}; and (2) fixed with zinc acetate for later analysis of sulphide. Samples of crusts formed on corroded wall rocks in the mixing zone were also collected in Stargate Blue Hole, South Andros.

Chemical analyses

Sulphide concentrations in zinc acetate-fixed samples were determined by standard iodometric titration. The results gave a consistent blank of 1 mg/l in the oxidized surface waters and was subtracted from all analyses. Sulphate concentrations were determined turbidimetrically using barium chloride. Mineralogical composition of the Stargate crusts was established using XRD and SEM-EDAX analysis.

Sulphur isotope analysis

Zinc acetate-fixed sulphide was reprecipitated as Ag_2S for analysis; SO_2 gas was prepared using the method of ROBINSON and KUSAKABE (1975). Barium sulphate precipitates were washed and dried; SO_2 gas prepared by the method of HALAS *et al.* (1982). The Stargate crust samples were scratched from the limestone surface using a steel dissecting needle; two separate sub-samples were collected from each sample. Calcite and gypsum were dissolved in 5% HCl solution and the residual pyrite filtered off, washed and dried. The dissolved SO_4^{2-} in the filtrate was precipitated with barium chloride after adjusting the solution pH to 1. The SO_2 gases for isotopic analysis were prepared using the procedures described above.

Colloidal S was extracted from filter papers by dissolution in tetrachloromethane and recovered by evaporation of the filtered solvent. This was prepared in the same way as the sulphides but the S/Cu_2O mixture was packed into a silica tube with a further excess of Cu_2O to oxidize any S migrating during combustion.
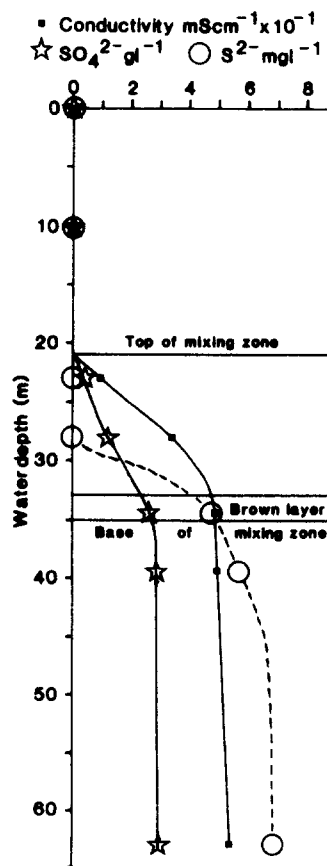

FIG. 2. Profiles of S species concentration and conductivity in Cousteau's Blue Hole.

face with saline water below. Sulphide concentrations increase sharply in the lower half of the mixing zone from zero to 5 mg/l. Sulphate concentrations increase steadily down through the mixing zone, paralleling the increase in conductivity. Samples from the base of the mixing zones in Ken's and No. 10 Blue Holes (Table 1) have similar SO_4^{2-} concentrations (2710 and 2420 mh/l, respectively) to the analogous level in Cousteau's Blue Hole, but have somewhat higher sulphide concentrations (31.1 and 15.7 mg/l, respectively).

Crusts on wall-rock in Stargate Blue Hole

The corroded wall-rock characteristic of the mixing zone in the Bahamas blue holes is often covered with a crust which is generally Fe-rich. This crust covers the pitted limestone surface and infills vugs caused by corrosion of more susceptible elements of the rock (e.g. ooids). In Stargate Blue Hole these crusts are well developed and XRD mineralogical analysis identified pyrite with some gypsum. X-ray amorphous Fe-oxides/hydroxides are also present (identified by EDAX analysis). Gypsum is present as fine needles and may be an artefact arising from oxidation of pyrite after the crusts were exposed to air. However, acicular gypsum has been reported as a primary feature from the mixing zone of an argillaceous feldspathic arenite aquifer (MAGARITZ and LUZIER, 1985). As our data (below) show that oxidation of sulphide takes place within the water column of Cousteau's Blue Hole, gypsum in the crusts may also be primary.

Isotopic data

Cousteau's Blue Hole. Aqueous sulphate sulphur isotope values are plotted in Fig. 3. Insufficient SO_4^{2-} for isotopic analysis was recovered from the upper 10 m (freshwater zone) but an interesting pattern in sulphate $\delta^{34}S$ emerges at greater depths. Samples from the saline zone (-39.5 at -61 m) have values around 19‰ CDT, close to normal open sea water. At the base of the mixing zone (-34.5 m) SO_4^{2-} is ^{34}S enriched ($\delta^{34}S = 22.1$‰ CDT); above this level, SO_4^{2-} becomes more ^{34}S-depleted ($\delta^{34}S = \approx 21$‰ CDT at -28 m and 18.6‰ CDT at -23 m). Two samples of colloidal S from the brown layer at the base of the mixing zone have isotopic compositions of $+0.5$ and -0.6‰ CDT (Table 1). Sulphide in the mixing zone was not analyzed because precipitates prepared from the relatively low concentrations were extremely impure.

Ken's and #10 Blue Holes. Sulphate sulphur isotope compositions in the mixing zone of both blue holes are slightly ^{34}S enriched compared to the deep saline water in Cousteau's Blue Hole ($\delta^{34}S = 21.0$ and 20.6‰ CDT, respectively, Table 1). By comparison, sulphide is isotopically far lighter, with $\delta^{34}S$ values between -25.9 and -28.0‰ CDT (Table 1).

Stargate crusts. Pyrite was analyzed from two samples and gypsum from one. In each case two sub-samples were prepared and analyzed separately and the results are presented in Table 1. The pyrite samples are isotopically light ($\delta^{34}S$ (‰ CDT) = -28.6 and -29.3 for sample 67-87; -35.3 and -34.8 for sample 7-87). Gypsum is also very light in sample 7-87, with $\delta^{34}S$ values for the two subsamples of -30.4 and -31.1‰ CDT.

DISCUSSION

Fractionations between S species

In the mixing zone at Cousteau's Blue Hole, there is a difference in S isotopic composition between aqueous SO_4^{2-} and colloidal S, in the same sample, of ~ 22‰. The mixing zones at Ken's and #10 Blue Holes show differences between SO_4^{2-} and sulphide

Table 1. Sulphur isotope compositions (‰ CDT). One and two are analyses of separate sub-samples

Sample No.	Depth (m)	Type	1	2
Ken's Blue Hole				
21-8-3-87	40	Aq. Sulphate	+21.0 (2710)	
21-8-3-87	40	Aq. Sulphide	−25.9 (12.1)	
No. 10 Blue Hole				
23-8-1-87	45	Aq. Sulphate	+20.6 (2420)	
23-8-1-87	45	Aq. Sulphide	−28.0 (14.7)	
Cousteau's Blue Hole				
076	34.5	Colloidal S°	+0.5	−0.6
Stargate Crusts				
67-87	25.5	Pyrite	−28.6	−29.3
7-87	22	Pyrite	−35.3	−34.8
7-87	22	Gypsum	−30.4	−31.1

Figures in brackets are concentrations in mg/l.

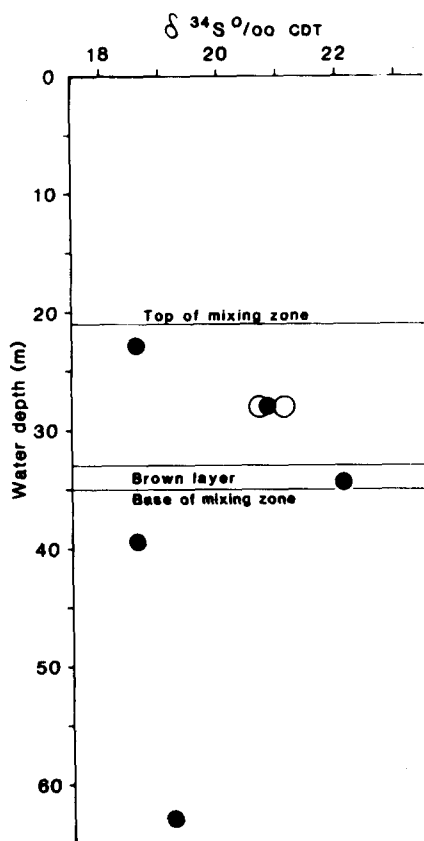δ ^{34}S $^{o}/oo$ CDT

FIG. 3. Profile of aqueous S sulphur isotopic composition in Cousteau's Blue Hole.

compositions of 46.9 and 48.6‰, respectively. These displacements are consistent with the large fractionations observed to accompany microbial reduction of SO_4^{2-} to S^0 or S^{2-} (e.g. NAKAI and JENSEN, 1964; CHAMBERS and TRUDINGER, 1979). These processes would result in ^{34}S enrichment of the residual SO_4^{2-}, a feature observed at the base of the mixing zone in Cousteau's Blue Hole, and which might be inferred from the heavier SO_4^{2-} δ^{34}S values from the mixing zones at Ken's and #10 Blue Holes, compared to deep saline water analyzed from Cousteau's Blue Hole.

Pyrite in the Stargate crusts also contains isotopically light sulphide (−28 to −35‰ CDT, Table 1) and probably formed by reaction of bacterially produced sulphide and the Fe-oxyhydroxide substrate of the crust. Gypsum in the same crust as pyrite (sample 7-87) has S isotope compositions slightly heavier than pyrite (by 4.9‰ and 3.7‰). Isotopic fractionations on oxidation of pyrite are relatively small (NAKAI and JENSEN, 1964), so at least the major part of the gypsum sulphate formed by pyrite oxidation, irrespective of whether this occurred *in situ* or on exposure to the atmosphere. However, for *in-situ* precipitation, whilst some of the heavier SO_4^{2-} in the gypsum may have been derived by incorporation of aqueous SO_4^{2-}, this contribution must have been

small. This indicates either that there was restricted penetration of water into the crusts or that the gypsum formed when the crust was exposed to SO_4^{2-}-poor freshwater.

Sulphur redox reactions in a mixing zone

As shown by the chemical profiles above (Fig. 2) the source of S within the mixing system is "seawater" SO_4^{2-} (δ^{34}S = ~19‰ CDT) derived from the underlying saline waters. At the base of the mixing zone the S isotopic composition of SO_4^{2-} is heavier by ~2‰, the result of bacterially mediated SO_4^{2-} reduction. This produces elemental S by the reaction.

$$2CH_2O + SO_4^{2-} = 2HCO_3^- + S^0 + H_2 \qquad (1)$$

at close to 0‰ CDT in Cousteau's Blue Hole; and sulphide,

$$2CH_2O + SO_4^{2-} = 2HCO_3^- + H_2S \qquad (2)$$

with δ^{34}S between −25.9 and −28.0‰ CDT in Ken's and #10 Blue Holes, respectively. The formation of these isotopically light reduced S species causes enrichment of ^{34}S in the residual SO_4^{2-}, as seen in the Coustau's Blue Hole profile (Fig. 3). The zone of SO_4^{2-} reduction appears to be localized in the brown-coloured layer of the mixing zone by supply of the reactants in reactions 1 and 2. Organic matter (represented by CH_2O) is supplied from biological and detrital inputs from the surface, while SO_4^{2-} is derived from the deep saline water.

In shallower water in the mixing zone, aqueous SO_4^{2-} becomes more ^{34}S depleted, approaching "sea water" values (Fig. 3). This results from the reoxidation of the isotopically light reduced S species produced by reactions 1 and 2 above (cf. sulphide profile, Fig. 2). As the isotopically light reduced species are oxidized, and SO_4^{2-} becomes the dominant S species, SO_4^{2-} compositions become similar to those of the original SO_4^{2-} source.

A chemical model for S in the mixing zone system

In this section we discuss reactions involving S in more detail, concentrating on their influence on H^+ and HCO_3^- concentrations and hence their interaction with the carbonate wall-rock.

Both SO_4^{2-} reduction reactions occurring in the Blue Holes (1 and 2 above) generate HCO_3^- alkalinity and will therefore tend to suppress corrosion of limestone wall-rocks. However, a number of other reactions generate acidity which acts corrosively. Fixing of sulphide by Fe.

$$H_2S + Fe^{2+} = FeS + 2H^+ \qquad (3)$$
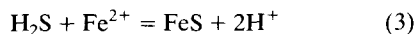
is one such reaction. The initial FeS is converted to pyrite by a mechanism which is poorly understood,

but probably involves the assimilation of S^0 (BERNER, 1984),
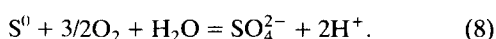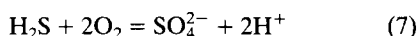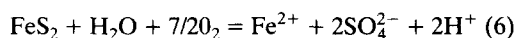
$$FeS + S^0 = FeS_2. \qquad (4)$$
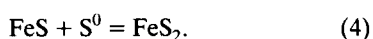
Pyrite formation appears to be restricted to crusts on the wall-rocks, possibly because only here can the acidity generated by reaction 3 be consumed by dissolution of calcite.

$$H^+ + CaCO_3 = Ca^{2+} + HCO_3^- \qquad (5)$$
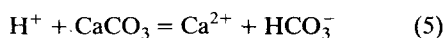
buffering pH and allowing FeS saturation to be maintained.

Acidity is also generated in the zone of oxidation of reduced S species by reactions,

$$FeS_2 + H_2O + 7/2O_2 = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (6)$$

$$H_2S + 2O_2 = SO_4^{2-} + 2H^+ \qquad (7)$$

$$S^0 + 3/2O_2 + H_2O = SO_4^{2-} + 2H^+. \qquad (8)$$

In the vicinity of the carbonate wall-rock this acidity is neutralized via reaction 5. The consequent local increase in both Ca^{2+} and SO_4^{2-} concentration could result in saturation with respect to gypsum,

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O \qquad (9)$$
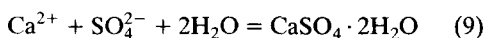
and hence the *in-situ* formation of gypsum in the Stargate crusts.

Rates of SO_4^{2-} reduction in the mixing zone

In the section above we outlined a geochemical model for S species in blue hole mixing zones. Here, we attempt to constrain the rates of the processes involved.

The data available from this reconnaisance study do not permit detailed modelling, but we are able to place some constraints on the rates of SO_4^{2-} reduction in the water column. Assuming the system to be at a steady state and that all SO_4^{2-} reduction takes place in the brown zone at the base of the mixing zone, a minimum estimate of the diffusional flux of H_2S required to maintain the sulphide concentration gradient at the base of the mixing zone in Cousteau's Blue Hole (Fig. 2) may be made. Initially, we assume diffusion through a static medium, for which Fick's first law of diffusion gives,

$$F_d = -D \cdot dC/dz,$$

where F_d is the diffusional flux, D is the diffusion coefficient (1.36×10^{-5} cm^2/s for H_2S in water at 25°C; HIMMELBLAU, 1964) and dC/dz the concentration gradient. The sulphide concentration profile at Cousteau's Blue Hole yields a flux of about 5.7×10^{-14} g cm^3/s or 1.4 mmol/m^2/a H_2S. This estimate ignores contributions from thermal diffusion effects which will be minor and reduce the flux because of the negative thermal gradient in a blue hole.

A more realistic scenario may be to consider vertical eddy dispersion, caused by tidal fluctuation, as the principal mechanism of mass transfer through the mixing zone. In such a case the flux required to maintain the observed sulphide concentration gradient would be far greater than for the static water model. Indeed, an experiment with the release of fluorescein dye in Stargate Blue Hole (P. L. SMART, unpublished data) showed lateral dispersions of 4 and 8 m in 20 min, inferring correspondingly rapid vertical dispersion.

The coefficient of vertical eddy dispersion (K_z) in the mixing zone is related to the vertical stability of the water column, largely a function of the density gradient,

$$N^2 = (g/p) \cdot (dp/dz),$$

where N is a criterion of vertical stability known as the buoyancy frequency or Brunt-Vaisala stability frequency, g the gravitational acceleration, p the density of water and dp/dz the density gradient, defined as positive in a downward sense. The value of N^2 for a blue hole mixing zone is very large, $\sim 10^{-1}$. LERMAN (1979) gives a plot of correlations between N^2 and K_z which shows that for $N^2 = 10^{-1}$, K_z lies between 10^{-2} and 10^{-3}; this would necessitate a H_2S flux of 0.1 to 1 mol/m^2/a to maintain the concentration gradient found in Cousteau's Blue Hole.

The rate of SO_4^{2-} reduction will be greater than the sulphide flux because of the component of SO_4^{2-} reduction producing S^0. Perhaps the assumption of a simple linear diffusion gradient is not an ideal model for the true situation where both oxidation and diffusion contribute to the decrease in H_2S concentration through the mixing zone. However, the most important but least constrained variable is the dispersion coefficient within a blue hole water column.

Impact on limestone corrosion

Again, the limited data from this reconnaissance study do not permit detailed modelling (this will be undertaken elsewhere using full chemical data on water samples), but some constraints can be placed on the contribution of acidity generated by S redox reactions to limestone corrosion.

In a closed system where SO_4^{2-} is reduced and the product oxidized back to SO_4^{2-} (e.g. reactions (2) and (7)), protons produced in reaction (7) are balanced by HCO_3^- alkalinity generated in reaction (2). However, the neutralization reaction,

$$H^+ + HCO_3^- = H_2O + CO_2 \qquad (10)$$
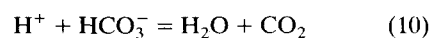
will increase pCO$_2$ and hence contribute to undersaturation with respect to carbonate minerals. Indeed, SMART *et al.* (1988) show just such an increase in pCO$_2$ associated with carbonate dissolution in a blue hole mixing zone. Furthermore, while H_2S concentrations are constant with depth below the mixing

zone (Fig. 2) and sulphide may only disperse upward, pCO_2 and HCO_3^- reach peak concentration in the mixing zone (SMART *et al.*, 1988) and may disperse both upward and downward. Hence fluxes of sulphide and HCO_3^- may become decoupled and oxidation of sulphide produces a net excess of protons in the upper part of the mixing zone. Additionally, fixing of sulphide as Fe-sulphides and their subsequent oxidation (reactions (3), (4) and (6)) will generate a further excess of protons over HCO_3^- ions and may occur where tidal fluctuation brings oxidized water into contact with wallrock crusts in the upper parts of the mixing zone.

Sulphur redox reactions are therefore able to produce an overall increase in limestone corrosion by both increasing pCO_2 (reaction 10) and by the oxidative generation of protons (reactions 3, 6, 7 and 8) where this can be decoupled from the production of HCO_3^- alkalinity. In this case, a first approximation to the maximum rate of carbonate dissolution by S redox processes can be derived from the calculated flux and the stoichiometry of reactions (7) and (5). For the case of the smallest flux estimate this corresponds to 280 mg $CaCO_3$ m²/a and for the largest 200 g $CaCO_3$ m²/a. At the present day in Cousteau's Blue Hole, where the water column at the depth of the mixing zone is about 30 m in diameter and oxidation takes place over a 5 m depth interval, the corresponding rates of wall-rock recession are 1.8 mm/10 ka for the static water model to 1200 mm/10 ka for the largest estimate, assuming eddy diffusion. Applied to the body of the aquifer, the maximum dissolution rate corresponds to an increase in porosity of 16% in 10 ka, comparable with estimates of 16–22% per 10 ka given for inorganic mixing corrosion by SANFORD and KONIKOW (1989).

SUMMARY AND IMPLICATIONS

Mass and isotopic analysis of S species in Bahamas Blue Holes demonstrate that bacterially mediated SO_4^{2-} reduction is taking place near the base of the freshwater–sea water mixing zone. Both sulphide and elemental S are produced and pyrite is formed where pH is buffered by calcite dissolution. Reoxidation of S species occurs in the overlying parts of the mixing zone and gypsum found in the pyritic crusts may originate from *in-situ* oxidation. These phenomena are analogous to those postulated for the formation of pyrite and gypsum in the Coos Bay coastal aquifer by MAGARITZ and LUZIER (1985), and similar processes are probably taking place in the mixing zone within the body of the Bahamian platform aquifer.

The rate of SO_4^{2-} reduction required to maintain the sulphide concentration gradient observed in Cousteau's Blue Hole is estimated as 1.4 mmol/m²/a for a static water column rising to a maximum of 1 mol/m²/a[1] if eddy dispersion is taking place. The

tidal flow in the Blue Holes and a dye dispersion experiment both suggest that the larger estimates are more probably correct. For this highest flux, reoxidation of reduced S species could for porosity generation in the aquifer at 16%/10 ka. This rate is significant when compared to rates proposed for dissolution by abiogenic mixing corrosion in similar situations (16–22%/10 ka; SANFORD and KONIKOW, 1989).

It is evident that bacterially mediated S redox reactions could contribute significantly to the development of porosity in freshwater–saline mixing zones in carbonate aquifers. Because rates of limestone dissolution by this mechanism could equal those associated with inorganic mixing zone corrosion, net dissolution rates could approach 30–35%/10 ka, which would generate significant reservoir porosity in a mixing zone on the timescale of a single sea-level stillstand.

Evidence for the operation of S redox processes in the formation of porosity in ancient mixing zones might come from the presence of crusts containing pyrite and/or gypsum similar to those found in the blue holes. The preservation potential of the crusts is, however, not great. Any crust exposed to oxidizing waters by a fall in sea level will lose pyrite by oxidation and any gypsum formed will be readily soluble. Only drowned mixing zones might be expected to preserve pyrite. In a study of uplifted horizontal mixing zone caves in eolian carbonates on San Salvador Island, Bahamas, VOGEL *et al.* (1990) found up to 30% gypsum encrustation in corroded wall-rock. They attributed this to evaporite formation since emergence, but a relict gypsum crust of mixing zone origin is an alternative possibility.

CONCLUSIONS

1. Bacterially mediated SO_4^{2-} reduction takes place within the mixing zone of Bahamian blue holes.

2. Reduced S species produced are reoxidized to SO_4^{2-} at shallower levels in the mixing zone.

3. Decoupling of sulphide and HCO_3^- fluxes produced by SO_4^{2-} reduction is possible, hence some parts of the mixing zone may experience enhanced carbonate mineral undersaturation due to acidity produced by sulphide oxidation.

4. Calculated maximum rates of SO_4^{2-} reduction (1 mol/m²/a[1]) are such that acidity produced by sulphide reoxidation may be a significant contribution to limestone dissolution compared to inorganic mixing corrosion.

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