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INORGANIC AND BACTERIOGENIC ORIGINS FOR SULFATE CRUSTS IN FLANK MARGIN CAVES, SAN SALVADOR ISLAND, BAHAMAS

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ABSTRACT

Two populations of gypsum, distinguished on the basis of sulfur isotopic composition, have been identified in crusts from the wall rocks of flank margin caves on San Salvador Island, Bahamas. One group has a restricted range of $\delta^{34}S$ values ($+21$ to $+23$ ‰ CDT) that are close to modern sea-water sulfate values. These are most probably derived by evaporation of vadose ground water contaminated by sea spray. The other group has values that range from -7 to -23 ‰ CDT. This isotopically light gypsum is depleted in ^{34}S relative to sea-water sulfate, which is characteristic of gypsum produced by oxidation of pyrite that was originally formed from bacteriogenic sulfide.

The isotopically-light gypsum indicates earlier bacterial production of sulfide from sulfate during formation of at least one flank margin cave within a freshwater lens. This implies that sulfate reduction may have been widespread in Bahamian carbonate island aquifers, and was not limited to open blue holes where it has previously been identified. Increased rates of cave wall-rock dissolution can result from reoxidation of bacteriogenic sulfide when it is exposed to oxygenated waters. Such enhanced dissolutional aggressivity may have influenced the development of flank margin caves.

INTRODUCTION

Cave wall-rock crusts containing sulfate in the form of gypsum have previously been described from flank margin caves developed in late Pleistocene eolianites on San Salvador Island, Bahamas by Vogel and others (1990). They proposed that the crusts formed by evaporative concentration of vadose ground water contaminated with sea spray. This evaporation occurred after the caves had become subaerial following a fall in sea level, with a concurrent fall in fresh-water lens position, in the Late Quaternary. However, an alternative explanation exists, as gypsum has also been reported from wall-rock crusts in zones of active dissolution in blue holes (Bottrell and others, 1991), where the gypsum forms by oxidation of bacteriogenic sulfide. According to this interpretation, the gypsum crusts formed by oxidation of original pyrite which formed while the flank margin caves were still flooded. Fortunately, sulfate-reducing bacteria fractionate the stable isotopes of sulfur during sulfide production, and therefore analysis of the $^{34}S/^{32}S$ ratio of sulfate from crusts can distinguish between these modes of origin.

The identification of bacterially-fractionated sulfur in gypsum crusts from flank margin caves is of significance for two reasons. First, it provides evidence for the activity of sulfate-reducing bacteria in parts of a past carbonate aquifer, in addition to modern blue holes where it has been described by Bottrell and others (1991). Prior to the results reported here, the blue hole data could have been considered atypical, as blue holes open to the surface are capable of receiving large amounts of organic material, which is not true of the rest of the aquifer. The data may indicate that sulfate-reducing bacteria are (and were) widespread in carbonate aquifers. Second, as Bottrell and others (1991) showed that the

hydrochemical effects of sulfate reducers in the halocline could significantly enhance wall-rock dissolution rates in blue holes, confirmation of their presence elsewhere in an aquifer implies that similar enhancement of limestone dissolution rates may be a factor in the formation of secondary porosity, including flank margin caves.

SETTING

With the single exception of a crust from a pit cave at +10m elevation, the crusts analyzed in this study are from flank margin caves in eolianite (dune) ridges on San Salvador Island, Bahamas (Figure 1).

These caves are generally at elevations between 0m and +6m above present sea level, and they formed at the discharging margin of a former fresh-water lens situated in the dune ridges during a past sea-level highstand (Mylroie and Carew, 1990). The morphology and mineralogy of many of these caves have been previously described (Vogel and others, 1990).

FIGURE 1: Map of San Salvador Island showing location of caves discussed in the text. Diagonal pattern represents interior lakes:
(RHP - Reckley Hill Pond
LL1 - South Little Lake
LL2 - North Little Lake
GTL - Great Lake
GNL - Granny Lake
SGNL - South Granny Lake
SRL - Storrs Lake
STL - Stouts Lake)
tidal creeks (PC - Pigeon Creek).
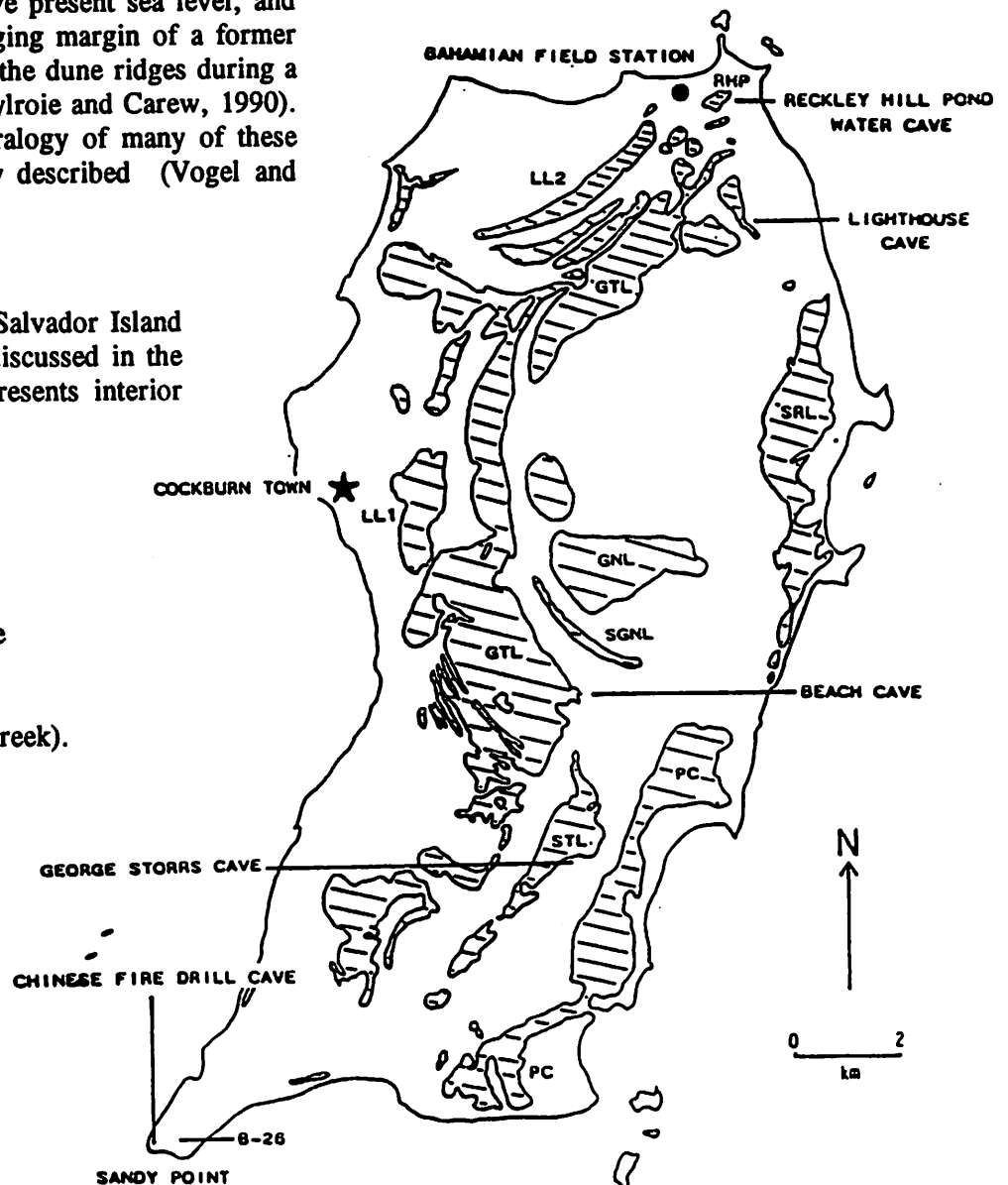
METHODS

Approximately one gram of wall-rock crust (identified by XRD as having significant gypsum) was coarsely crushed and dissolved overnight in 0.5 molar HCL. The insoluble residue was removed by filtering, and the filtrate was adjusted to a pH of 2.5 and heated to 70 °C prior to precipitation of sulfate as $BaSO_4$. After aging overnight at 40 °C, the $BaSO_4$ was collected by filtering onto a $0.45 \mu m$ membrane filter, and then dried.

SO_2 gas was prepared from $BaSO_4$ using the method of Halas and others (1982), and analyzed using a VG SIRA10 gas source isotope-ratio mass spectrometer; the raw data were corrected using standard procedures (e.g. Coleman, 1980).

RESULTS

The results of the sulfur isotopic analyses are presented in Table 1 in standard delta form relative to the Canyon Diablo Troilite (CDT) standard, i.e.: $\delta^{34}S_{sample} = ((R_{sample}/R_{CDT}) - 1) \times 1,000$ ‰ where R_{sample} and R_{CDT} are the $^{34}S/^{32}S$ of the sample and CDT standard, respectively. The data fall into two distinct groups, one that has a narrow range of positive values (+19.9 to +23.0 ‰ CDT), and another having a wider spread of negative values (-7.5 to -23.4 ‰ CDT). The former group of ^{34}S-enriched values is close to that of modern sea-water sulfate (approximately +20 ‰ CDT), while the latter ^{34}S-depleted values are typical of biogenically fractionated sulfur (Chambers & Trudinger, 1979).

DISCUSSION
Isotopically-Heavy Gypsum

Samples from the majority of locations studied have $\delta^{34}S$ values that are typical of modern sea water values, or are slightly heavier (Table 1).

These values suggest that sea water is the ultimate source of the sulfate in these gypsum crusts, but that some minor modification of sulfate $\delta^{34}S$ has taken place. The modifications probably result from slight fractionation of sulfate during crust formation, as the heavier ^{34}S isotope is, to a small extent, preferentially incorporated into the solid phase (Raab and Spiro, 1991). It is also possible that the ground-water sulfate may have undergone some bacterial reduction that removed a small amount of ^{32}S-enriched sulfate before crust formation. However, it is unlikely that reduction took place in the vadose zone, as water there is too well oxygenated for sulfate-reducing bacteria (which are obligate anaerobes) to function.

There are two possible sources of ground-water sulfate which might produce gypsum crusts with near sea-water $\delta^{34}S$ composition on San Salvador. One is direct contamination of vadose ground water by sea spray; the other is from ground water derived from the ocean directly, or from saline and hypersaline lakes (all at sea level) in the island's interior (in which sulfate is concentrated from sea water by evaporation and has $\delta^{34}S$ similar to sea water). Clearly one, or both, of these sources supplied sulfate for formation of gypsum crusts in many San Salvador caves.

ANALYSIS OF $\delta^{34}S$ FROM SAN SALVADOR CAVES

Sample	Site Description	Elevation	Gypsum $\delta^{34}S$
SS-B26-1	Vadose Pit Cave B-26, Sandy Point	10 m	+19.9
SS-BC-40	Beach Cave, Great Lake	3 m	+21.2
SS-BC-41	Beach Cave, Great Lake	3 m	+21.0
SS-CF-51	Chinese Fire Drill Cave, Sandy Point	2 m	+20.9
SS-CF-53	Chinese Fire Drill Cave, Sandy Point	2 m	+23.0
SS-GS-19	George Storrs Cave, Stouts Lake	3 m	+21.2
SS-LHC-691	Lighthouse Cave, Dixon Hill	1 m	+20.3
Reckly Hill Pond Water Cave, Reckly Hill			
SS-RW-60	Rear of main chamber	0.25m	-7.5
SS-RHPC-591			
Front-A	Center of main chamber	2.0m	-23.0
Front-B	Center of main chamber	1.5m	-23.4
Front-C	Center of main chamber	1.0m	-22.5
Back	Rear of main chamber	0.25m	-19.2

TABLE 1. $\delta^{34}S$ values for samples from caves on San Salvador Island, Bahamas. Sample SS-B26-1 is from a vadose pit cave, the rest are from flank margin caves. See Figure 1 for site locations. Elevations in meters above sea level.
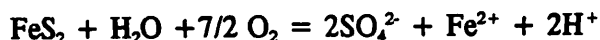
While it is impossible to discount ocean or lake sources entirely, the following factors make it unlikely. First, sample B26-1 (+19.9 °/$_{oo}$ T) is from a pit cave located at an elevation (+10m) well above the influence of present or past ocean and lake waters. For that sample, sea spray contamination of the vadose zone is the only viable sulfate source. Second, only two of the caves studied extend to modern sea level, the rest are dry and free of ocean or lake influence under current conditions. Of the two caves that do extend to modern sea level, the gypsum crusts from one of them (Reckley Hill Pond Water Cave) contains only isotopically-light crusts.

The isotopically-heavy population of gypsum crusts therefore seem most likely to have resulted from contamination of the vadose zone of the carbonate aquifer with sulfate derived from sea spray. The data demonstrate that these crusts formed after the caves were drained by a fall in sea level, and that evaporative concentration in the subaerial flank margin caves was sufficiently intense that sulfate and calcium concentrations were elevated above gypsum saturation.

Isotopically-Light Gypsum

Gypsum crusts from one locality on San Salvador have markedly different sulfur isotope compositions (Table 1). These isotopically-light values are characteristic of sulfur which has been isotopically fractionated by sulfate-reducing bacteria. These values indicate that some, if not all, of the sulfate in these crusts arose from oxidation of bacterially-produced sulfide. All but one of the values from the Reckley Hill Pond Cave site (-19.2 to -23.4 °/$_{oo}$ CDT) are close to values for bacterial sulfide reported from blue holes (-25 to -35 °/$_{oo}$ CDT) by Bottrell and others (1991). The somewhat heavier value from sample RW-60 (-7.5 °/$_{oo}$ CDT) may represent a mixture of oxidized bacteriogenic sulfide, and sulfate from vadose ground water contaminated by sea spray.

It is interesting to note that Reckley Hill Pond Water Cave, with isotopically-light sulfate crusts, is also the only sampled cave where substantial breakdown (collapse) has occurred. This breakdown may well be the result of weakening of the cave walls by both crystal wedging, and by oxidation of original bacteriogenic sulfide (probably originally present as pyrite) in the crusts to sulfate, a reaction which generates acidity:

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

Such acidity may have resulted in dissolution that weakened the wall rock of the cave.

Wider Implications

The bacterial reduction of sulfate to produce the original isotopically-light sulfide (pyrite) in the wall-rock crusts must have occurred during the time these flank margin caves were forming at the freshwater-saline interface (halocline) of the island's aquifer, during a past sea-level highstand. At that time the chemical environment in the cave and adjacent wall rock would have been similar to that in modern blue holes where bacterial sulfate reduction has been documented (Bottrell and others, 1991). Subsequently, as sea level fell and the caves were drained, conditions would always have been so oxidizing that sulfate reduction would be impossible. Perhaps the most important conclusion of this work is that it demonstrates that sulfate-reducing bacteria were active at the discharging margin of the island's former fresh-water lens. Now that their activity has been demonstrated both there and in blue holes it seems likely that these bacteria permeate the halocline throughout carbonate island aquifers. That bacteria can permeate the carbonate aquifer of islands was demonstrated by Mylroie and Balcerzak (in press), who discovered short-lived avian bacteria throughout the fresh-water lens of San Salvador.

The effects of sulfate reducers on water chemistry and dissolution rates in carbonate aquifers have been modelled by Bottrell and others (1991). They showed that, in some cases, rates of limestone dissolution attributable to sulfate reducers could equal that calculated for simple inorganic mixing corrosion (e.g. Sanford & Konikow, 1989), thereby doubling the dissolution potential in this environment. It is likely that enhanced rates of dissolution associated with the activity of sulfate reducers may have played a significant role in the development of flank margin caves during the short periods of sea-level highstands of the late Pleistocene. Based on Quaternary sea-level curve amplitudes and isostatic subsidence rates, it has been demonstrated (Mylroie and others, 1991; Carew and Mylroie, 1992) that the flank margin caves of the Bahamas could have formed only during the approximately 10,000 to 15,000 year time window associated with the oxygen isotope substage 5e (Sangamon Interglacial) highstand. Models based on

inorganic mixing alone (Sanford and Konikow, 1989) do not yield sufficient dissolution to produce the known volume of many Bahamian flank margin caves. Oxidation of bacteriogenic sulfide, coupled with inorganic mixing, offers a means to accomplish the dissolution of flank margin caves within the given time constraints.

CONCLUSIONS

Sulfur isotope analyses of gypsum crusts from cave walls on San Salvador Island define two distinct sulfate populations. Isotopically-heavy sulfate resulted from evaporative concentration of sea-spray contaminated ground water in the vadose zone after flank margin caves were drained by a fall in sea level. Isotopically-light sulfate was produced by oxidation of bacteriogenic sulfide present in the wall-rock crusts. The sulfide (probably pyrite) was produced by sulfate-reducing bacteria that were active when the caves formed phreatically near the ground-water halocline. These isotopically-light crusts indicate the presence of sulfate-reducing bacteria at the distal margin of past fresh-water lenses. Further, enhanced rates of limestone dissolution associated with bacterial activity may have been important in the rapid formation of flank margin caves.

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