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ISOTOPIC GEOCHEMISTRY OF A MID-PROTEROZOIC EVAPORITE BASIN: BALMAT, NEW YORK

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ABSTRACT. Lenses of Proterozoic meta-evaporitic anhydrite as much as 60 m thick occur in a 1150 to 1300 Ma Grenville Series marble sequence near Balmat, New York. $\delta^{34}S_{anhy}$ values in the oldest lens average 8.2 permil; progressively younger lenses average 19.6, 27.2, 26.7, and 19.1 permil. The thickest and isotopically heaviest lens displays coincident upsection increases in $\delta^{34}S_{anhy}$ (24.1–30.2 permil) and $\delta^{18}O_{anhy}$ (19.8–22.5 permil) values. These increases and the overall ^{34}S enrichment of the anhydrite indicate that anhydrite precipitation was concurrent with large-scale bacterial sulfate reduction in the depositional basin. A similar increase in the $\delta^{34}S$ values of biogenic pyrite (total range, −31.6 to 12.9 permil) and a decrease in the $\delta^{13}C$ values of marble carbonate (total range, −3.7 to 5.1 per mil) are also consistent with large-scale bacterial sulfate reduction. The high $\delta^{18}O_{anhy}$ and low $\delta^{34}S_{anhy}$ values of the oldest lens may reflect extensive oxidation of biogenic H_2S.

The arid climate and high evaporation rates implied by evaporite deposition would result in ^{18}O enrichment of the basin waters and the carbonates precipitated from them. Carbonate in the marbles *is* ^{18}O-enriched (22.6–26.6 permil) with respect to other marbles of the Grenville Series. Quartz from metaquartzite layers has high $\delta^{18}O$ values (25.3–27.9 permil), suggesting a chert protolith.

The evidence of arid climate and the variability and ^{34}S-enrichment of the anhydrite imply that the Balmat environment was a closed or restricted basin in which evaporation and bacterial sulfate reduction combined to produce a ^{34}S-enriched, sulfate-rich brine. Holser (1977) proposed that such brines might generate abrupt worldwide increases in the $\delta^{34}S$ of marine sulfate. However, Holser could only note these abrupt increases and hypothesize that they recorded the addition of a ^{34}S-enriched, sulfate-rich brine to the ocean. The isotopic systematics of the anhydrite imply that the Balmat depositional basin was restricted and may have been a "holding tank" for the accumulation of such a brine.

Spent fluids from synsedimentary hydrothermal activity at Balmat may have provided iron for the precipitation of ^{34}S-depleted biogenic pyrite. Similar upsection ^{34}S-enrichments of sedimentary pyrite are found with mineralization at McArthur River, Australia and Outokumpo, Finland. This suggests that submarine hydrothermal metal input can promote ^{34}S-enrichment of seawater sulfate by continually removing biogenic H_2S from the basin.

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INTRODUCTION

Metasediments and metavolcanics of the mid-Proterozoic Grenville Series cover much of southeast Canada and northern New York. In the Adirondack Lowlands of northwestern New York the Grenville Series is composed largely of pelitic and metavolcanic schists and gneisses, minor amphibolites, and two thick marbles. Near Balmat Corners, New York, the younger of these marbles contains thick accumulations of anhydrite (deLorraine and Dill, 1982, and references therein). If these bedded anhydrites are evaporitic, they are among the oldest preserved in the geologic record. A hydrothermal origin is also possible, however, because this marble also hosts the well-known Balmat-Edwards stratiform Zn-Pb ore deposits (deLorraine and Dill, 1982: Whelan, Rye, and deLorraine, 1984).

Holser (1977) proposed that sudden peaks in the $\delta^{34}S$ value of seawater sulfate, as recorded by marine evaporites, reflect addition of ^{34}S-enriched, sulfate-rich brines to the oceans and that these brines accumulated in restricted basins where bacterial reduction caused ^{34}S-enrichment of the sulfate. Our stable isotope studies of the bedded anhydrite, of the marble carbonate, of non-ore pyrite in the marble sequence, and of quartz from metaquartzite horizons support an evaporitic origin of the anhydrite and suggest deposition in a restricted basin similar to that proposed by Holser (1977). We also expand upon the idea presented by Whelan, Rye, and deLorraine (1984) that input of iron from hydrothermal activity to isolated or restricted marine basins can greatly amplify the effects of bacterial sulfate reduction on the $\delta^{34}S$ values of sulfate in a basin. This amplification may be an important, and missing, piece of Holser's (1977) model.

Sulfur isotope systematics of ore and non-ore sulfides, barite, and marine sulfate in the Anvil Range, Yukon (Goodfellow and Jonasson, 1984; Shanks and others, 1987) suggest that the Selwyn Basin is a possible analog of the marble-hosted anhydrite and Zn-Pb deposits at Balmat.

REGIONAL GEOLOGY

The Adirondack Lowlands of northwest New York (fig. 1) are underlain by 5 to 6 km of Grenville Series metasediments and metavolcanics (Engel and Engel, 1953a and b). The Grenville Series consists primarily of gneisses and marbles with minor amphibolites and quartzites which present evidence suggests were deposited 1300 ± 200 Ma (Barton and Doig, 1974; Fletcher and Farquhar, 1977; Grant and others, 1986). Grant and others (1986) infer that deposition of the anhydrite-bearing marble at Balmat probably occurred between 1150 and 1300 Ma.

The Grenville Series stratigraphy in the Adirondack Lowlands consists of Upper and Lower Marbles separated by the roughly 750-m-thick Popple Hill Gneiss and underlain by the Hyde School Gneiss

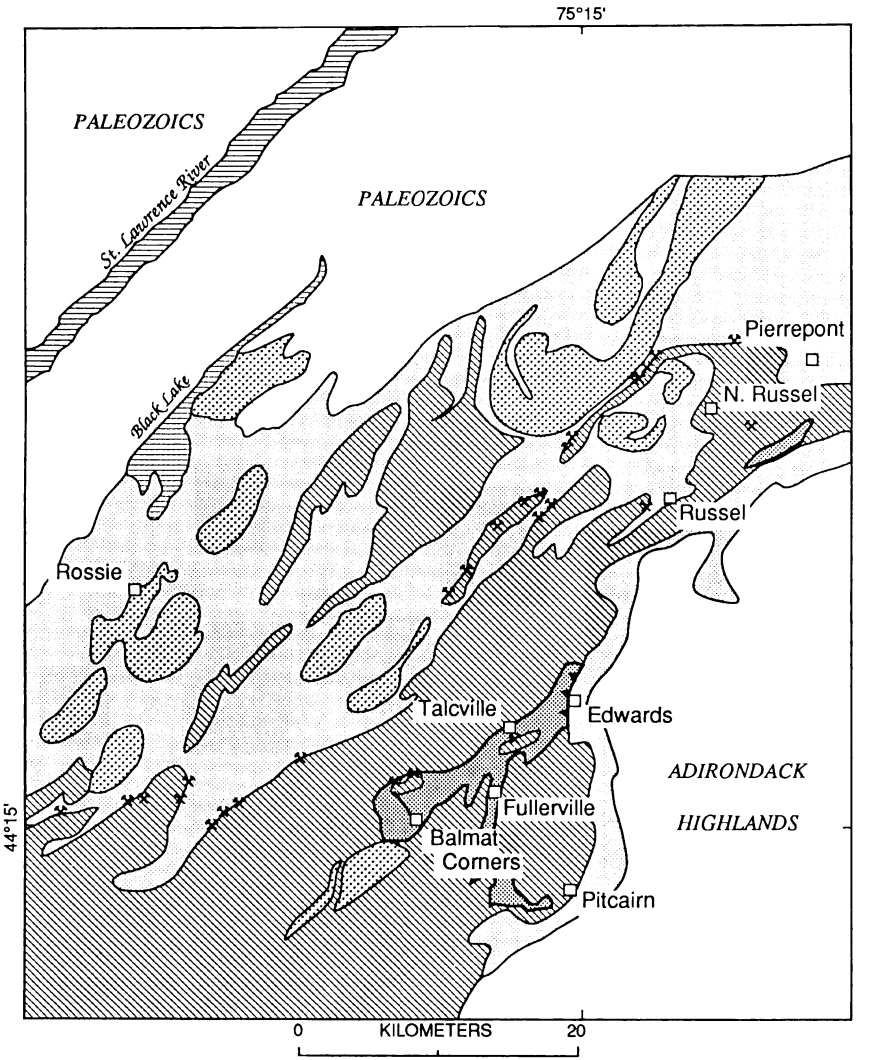


Fig. 1. Generalized geologic map of the Adirondack Lowlands. Diagonally lined = paragneisses, mainly the Popple Hill Gneiss but including unit 2 of the Upper Marble ≈2 km north-northwest of Balmat Corners and the Pleasant Valley Gneiss just south of Talcville. Dotted pattern = granitic gneisses and metaintrusives; the body south of Rossie is metaintrusive. Lightly shaded = Lower Marble. The darker shaded, boldly outlined areas = the Upper Marble. Mine symbols show the locations of metasedimentary iron sulfide deposits discussed in Prucha (1957). Line running from the unit 2 outcrop to Balmat Corners shows the orientation of the cross section of figure 2. Map compiled from figures in Carl and Van Diver (1975), Buddington, Jensen, and Mauger (1969), and recent mapping studies by deLorraine (in preparation).

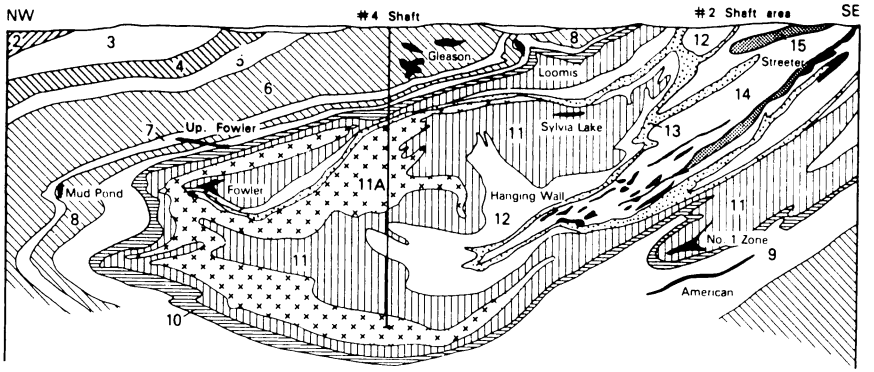
(fig. 2). The marbles are metamorphosed carbonate (largely dolomitic) sediments. Engel and Engel (1953b) suggested that the Popple Hill Gneiss (their Major Gneiss), had a shale protolith. Carl (1988), however, argues for a protolith of dacitic volcanics with minor pelitic horizons. The Hyde School Gneiss is composed of leucogranitic metarhyolites and metadacitic tuffs (Carl and Van Diver, 1975). This stratigraphic interpretation contrasts with that of Wiener and others (1984) who correlated the Upper and Lower Marbles and thus built a stratigraphy with only one marble.

Amphibolite to granulite facies metamorphism of the Grenville Series occurred about 1150 Ma (Doe, 1962; Krogh and Hurley, 1968; Grant and others, 1986; Mezger, Bohlen, and Hansen, 1988), with peak metamorphic conditions at Balmat of about 6.5 kb and 625°C (Bohlen and Essene, 1977; Brown, Essene, and Kelly, 1978). Four phases of deformation are recorded in the Grenville Series in the Adirondack Lowlands. The initial deformation produced large-scale, nappe-like, recumbent folds (Brown and Engel, 1956; Foose, ms; Romey and Jacoby, 1978; deLorraine, ms; deLorraine and Dill, 1982; Wiener and others, 1984). Overturned second-phase northeast-striking isoclines refolded the strata and produced the pronounced northeast-southwest outcrop pattern of the Lowlands (fig. 1). Two upright to steeply-dipping foldsets—the earlier tight to isoclinal and north-northeast trending, the later open and northwest trending—interfered with the earlier folds, forming regional hook-shaped and modified dome and basin patterns. Plastic flow has locally thickened or thinned the more deformable units, such as the marbles.

The Grenville Series of the Lowlands is host to some extraordinary iron-sulfide-rich metasediments. Buddington, Jensen, and Mauger (1969) provided the following observations of these rocks: (1) they occur in four zones—within the Lower Marble, in the Popple Hill Gneiss just above the Lower Marble, within metagabbro-amphibolite hosted by the Popple Hill Gneiss, and just above the base of the Upper Marble (unit 2—see immediately following discussion of the Upper Marble). These zones are typically 3 m in thickness and ≈10 percent pyrite but can reach 10 m and 70 percent pyrite (Prucha, 1957). Pyrite is the dominant sulfide, although pyrrhotite is common, and, rarely, sphalerite. Quartz is the dominant gangue, commonly with some feldspar, sericite, and chlorite. Some disseminated graphite is always present, and most zones have accessory dravite. Buddington, Jensen, and Mauger (1969) attribute these zones to metamorphism of pyritic organic-rich sediments.

THE UPPER MARBLE

The village of Balmat is at the southwest tip of a body of Upper Marble that extends northeast to the village of Edwards, near Cedar Lake. A canoe-shaped outlier of the same marble is exposed south of Pierrepont, some 46 km northeast of Balmat (fig. 1). In the vicinity of Balmat, the Upper Marble has a present thickness of ≈1000 m, which is



A.

B.

UNIT	LITHOLOGY	THICKNESS
16	Median gneiss: quartz-biotite-feldspar	60
15	Phlogopitic silicated calcitic marble	10
14-C	Serpentinous dolomitic and calcitic marble	35
14-B	Calcitic marble; quartz augen	40
14-A	Banded quartz-diopside rock; minor dolomite	35
13	Talcose tremolite schist; anhydrite	25
12	Dolomitic marble, minor diopside; minor anhydrite	45
11, 11A	Quartz-diopside, dolomitic, and calcitic marbles; anhydrite	90
10	Talcose diopside rock with biotite; anhydrite	15
9	Dolomitic marble	20
8	Quartz-diopside and dolomitic marbles	40
7	Fetid, graphitic dolomitic marble	35
6	Quartz-diopside and dolomitic marbles; quartzite; anhydrite	165
5	Dolomitic marble	50
4	Quartz-diopside and dolomitic marbles	90
3	Dolomitic marble	120
2	Pyritic quartz-mica-feldspar schist	30
1	Dolomitic marble	120

UPPER MARBLE
POPPLE HILL GNEISS
LOWER MARBLE
HYDE SCHOOL GNEISS

Fig. 2. Geology of the Upper Marble: (A) is a cross section of the marble belt showing the locations of many of the Zn-Pb orebodies; where unit 11 is >50 percent anhydrite, it is patterned with x's; (B) shows the stratigraphic sequence of the Upper Marble. Both figures courtesy of Zinc Corporation of America.

probably within 10 percent of the original thickness (Wm. deLorraine, personal commun.). Deformation has thinned the Upper Marble to only ≈100 m in the vicinity of Edwards. Brown and Engel (1956), Lea and Dill (1968), and deLorraine (ms) showed that the Upper Marble is at the core of a northeast striking, north-northwest plunging recumbent synform overturned to the southeast, the Sylvia Lake syncline, which is hinged near Balmat (figs. 1 and 2A).

Detailed mine mapping and exploration drilling allowed Brown and Engel (1956) to establish the stratigraphy and unravel the complex structure of the Upper Marble. The sixteen stratigraphic units (numbered from oldest to youngest) are, in general, an alternation of fairly pure dolomitic and quartzose calc-silicate-rich dolomitic marble (fig. 2B). Units 1, 3, 5, 7, 9, and 12 are typically >95 percent dolomite. They may contain up to 1 percent of quartz, potassium feldspar, diopside, tremolite, talc, phlogopite, graphite, or pyrite. Units 4, 6, 8, and 11 contain >40 percent quartz and (or) diopside thinly interlayered with dolomite. Variable amounts of tremolite, talc, phlogopite, potassium feldspar, graphite, or pyrite occur as accessories. The ratio of quartz to diopside in the quartzose calc–silicate–rich units is highly variable, ranging from <1 to >10.

Metamorphism has obscured or obliterated most primary sedimentary structures that might clarify the depositional setting of the Upper Marble. Finely laminated and persistent layers of quartz + diopside that may record bedding are common, but no evidence of cross-bedding is preserved. Stromatolites have been identified in unit 4 (Isachsen and Landing, 1983) and unit 11.

The remaining units are: unit 2, a pyritic, graphitic quartz–mica–potassium feldspar–chlorite schist (locally garnet- and (or) sillimanite-bearing); unit 10, a distinctive pea-green serpentine–talc–diopside rock; unit 13, an anthophyllite–tremolite–talc schist (locally anhydrite-bearing); units 14 and 15, which are serpentinous calcitic and dolomitic marbles; and unit 16, a migmatitic potassium feldspar–quartz–mica paragneiss.

Lenses and layers of anhydrite occur in unit 6 and units 10 through 14. Medium- to coarse-grained anhydrite composes 50 to 100 percent of these horizons. Brownish in unit 6, elsewhere the anhydrite is usually pale to deep lavender. Quartz and diopside may be present, with minor tremolite, talc, calcite, phlogopite, and pyrite. The thickest lenses occur near the bases of unit 6 (15–20 m) and unit 11 (40–60 m). Plastic deformation has thickened the lens in unit 11 to as much as 300 m in the hinge zone of the Fowler syncline. This lens is mapped as 11A, a subunit of unit 11 (figs. 2A, B, and 3). The anhydrite lenses in units 10, 12, 13, and 14 are 1 to 15 m thick.

ANALYTICAL PROCEDURES

The majority of samples came from drill core. This circumvented complications from surficial weathering which dissolves anhydrite and

oxidizes sulfides, and sparse outcrop. Samples from drill core can also be located more accurately within the stratigraphic units. A few samples came from underground exposures.

Some anhydrite samples were purified by standard heavy liquid and magnetic separation methods and then converted to Ag_2S by the technique of Thode, Monster, and Dunford (1961). The majority of anhydrite samples were dissolved in 0.6N hydrochloric acid or 1N NaCl solution (for oxygen isotope analysis) and reprecipitated as $BaSO_4$. Sulfur isotope determinations were performed on the $BaSO_4$ by techniques described by Holt and Engelkemeir (1970) and Bailey and Smith (1972). Oxygen isotope analysis of $BaSO_4$ followed the procedure of Nehring, Bowen, and Truesdell (1977).

Carbonate analyses were performed on pulverized splits of whole marbles. Most marbles were so overwhelmingly dolomitic or calcitic that no significant error was introduced by treating the whole marble splits as pure separates. Marble samples with calc-silicate minerals were avoided because of possible complications from metamorphic decarbonation reactions. Carbonate CO_2 was extracted by reaction with 100 percent H_3PO_4 at 25°C (McCrea, 1950).

Pyrite occurs commonly within the marble sequence as scattered trace disseminations of small (0.1-2.0 mm) grains. These pyrite grains were generally cubic or pyritohedral, suggesting recrystallization during metamorphism, and bore no apparent association with the Zn-Pb orebodies. Pyrite concentrates were made by heavy liquid separations and then purified in warm 0.6N hydrochloric acid. Sulfur dioxide was extracted from pyrite and Ag_2S by reaction with copper oxides at $\approx$1025°C (Fritz, Drimmie, and Nowicki, 1974).

The metaquartzites are pure and quite coarse-grained in thin section, with individual grains sometimes exceeding a centimeter. Sutured grain boundaries suggest that the coarseness probably reflects metamorphic recrystallization. Quartz samples were pulverized and treated with warm 0.6N hydrochloric acid to remove any possible carbonate traces. Oxygen isotope analysis of quartz followed standard procedures (Clayton and Mayeda, 1963).

Isotopic compositions are reported as the permil deviation of the sample isotopic composition from that of the appropriate international standard; CDT (for sulfur), SMOW (for oxygen), or PDB (for carbon). Reproducibility (1 σ) is within $\pm$0.1 permil for sulfides, carbonates, and silicates; and within $\pm$0.2 permil for sulfates.

RESULTS

Recrystallization during the metamorphism of the Upper Marble resulted in extensive isotopic exchange between minerals (Whelan, Rye, and deLorraine, 1984). That study demonstrated that sulfur isotopic equilibration between sulfide and sulfate minerals was virtually complete within hand specimens but not between samples separated by as little as 1 m, and that oxygen isotope exchange had occurred between

intimately mixed anhydrite and carbonate. These findings dictated cautious selection of samples and interpretation of results to ensure that conclusions concerning the depositional environment of the carbonate sediments were drawn only from samples that had retained their pre-metamorphic isotopic compositions. When possible, only samples where the desired mineral had no other minerals with which to exchange were studied. Despite these precautions, however, it is possible that the isotopic compositions of the metaquartzites and non-ore pyrite in the marbles reflect fluid-mediated exchange with carbonate and anhydrite, respectively, during metamorphism. These possibilities are discussed in more detail in the results and discussion sections.

$\delta^{34}S$ and $\delta^{18}O$ values of anhydrite.—Seventy-five anhydrite $\delta^{34}S$ values ($\delta^{34}S_{anhy}$), predominantly from units 6 and 11A, but including typical samples from units 10, 12, 13, and 14, are reported in table 1 and plotted on figures 3, 4, and 6. $\delta^{34}S_{anhy}$ values rise abruptly from an average of 8.2 permil in unit 6 (range, 4.2–10.2 permil) to 19.6 permil in unit 10 (range, 18.3–21.2 permil), 27.2 permil in unit 11A (range, 24.1–30.2 permil), and 26.7 permil in unit 12 (range, 26.4–27.1 permil), then decrease to 19.1 permil in units 13 and 14 (range, 16.7–21.0 permil) (figs. 3 and 4).

The $\delta^{18}O$ values of seven anhydrite samples ($\delta^{18}O_{anhy}$), two from unit 6 (19.0 and 19.1 permil) and five from unit 11A (ranging from 19.8 to 22.5 permil) are also listed in table 1.

Anhydrite from the Upper Marble without close stratigraphic control was sampled from cored drillholes sited near the villages of Talcville, Fullerville, and Edwards. The $\delta^{34}S_{anhy}$ values of these samples range from 9.0 to 26.7 permil (table 1).

Anhydrite occurs locally within the Lower Marble, but as a minor constituent only. Lower Marble anhydrite $\delta^{34}S$ and $\delta^{18}O$ values ranged from 9.5 to 21.8 permil and from 16.7 to 22.2 permil, respectively (table 1).

The much lower $\delta^{34}S_{anhy}$ values of unit 6 and the positively correlated increases of the $\delta^{34}S_{anhy}$ and $\delta^{18}O_{anhy}$ values from the bottom to the top of unit 11A (figs. 3 and 4) distinguish Upper Marble anhydrite from all other studied anhydrite occurrences.

$\delta^{34}S$ values of non-ore pyrite.—Disseminated pyrite, and (rarely) traces of sphalerite, is widely distributed within the Upper Marble. Typically comprising much less than 1 percent of the marbles, pyrite (±pyrrhotite) concentrations often exceed 10 percent in unit 2 and the Pleasant Valley Gneiss. "Non-ore" pyrite is that in parts of the metasedimentary section free of evidence of hydrothermal activity. It is probably sedimentary or diagenetic and not directly related to the formation of the Zn-Pb orebodies. Doe's (1962) findings of much higher cobalt and nickel contents in the non-ore pyrite than in the orebody pyrite support this conjecture. Non-ore pyrite is usually associated with graphite and has $\delta^{34}S$ values ($\delta^{34}S_{sedpy}$) which range from −31.6 to 12.9 permil (table 2 and fig. 4), common attributes of pyrite formed from the bacterial reduction of sulfate.

TABLE 1

$\delta^{34}S$ and $\delta^{18}O$ values (permil) of bedded anhydrite from the Upper and Lower Marbles. Sample traverses within drill holes are designated by lower case letters, in alphabetic order from stratigraphic top to bottom. Depths (m) below the top of the lenses are shown in parentheses

Sample No.	Unit	$\delta^{34}S$(‰)	$\delta^{18}O$(‰)
Upper Marble Samples			
A-2	14	20.1	
A-3	13	16.7	
A-4	13	21.0	
A-5	13	17.1	
A-6	12	25.8	
A-7a (0.6)	12	26.7	
A-7b (6.1)	12	27.1	
A-7c (12.5)	12	26.4	
A-8a (0.0)	11A	30.2	22.5
A-8b (7.0)	11A	28.5	
A-8c (13.1)	11A	26.7	
A-8d (19.2)	11A	29.0	22.3
A-8e (23.2)	11A	28.0	
A-8f (25.3)	11A	28.6	
A-8g (31.4)	11A	27.6	
A-8h (40.5)	11A	25.5	
A-8i (46.6)	11A	28.3	
A-8j (52.7)	11A	28.9	
A-8k (64.9)	11A	27.7	
A-8l (77.1)	11A	25.9	
A-8m (89.3)	11A	25.8	
A-8n (97.8)	11A	26.4	21.1
A-8o (102.1)	11A	27.0	
A-9a (0.0)	11A	29.4	
A-9b (7.6)	11A	29.0	21.8
A-9c (19.8)	11A	26.8	19.8
A-9d (32.0)	11A	25.1	
A-19a (0.0)	6	8.8	
A-19b (3.4)	6	8.5	
A-19c (6.4)	6	8.4	
A-19d (8.5)	6	8.9	
A-19e (11.6)	6	5.4	
A-20a (0.0)	6	8.8	
A-20b (7.6)	6	8.7	
A-20c (9.1)	6	8.8	
A-20d (15.2)	6	7.6	
A-21	Fullerville	20.1	
A-22	Fullerville	19.0	
A-23	Talcville	26.7	
A-24	Talcville	20.4	
A-25	Talcville	18.5	
A-26	Edwards	24.4	
A-27	Edwards	9.0	
A-28	Edwards	9.4	
A-29	Edwards	10.3	
A-30	Edwards	17.4	
A-31	Edwards	17.0	
A-32	Edwards	14.5	
A-9e (42.7)	11A	24.8	
A-10a (0.0)	11A	28.7	
A-10b (7.6)	11A	29.4	
A-10c (18.3)	11A	28.6	
A-10d (33.5)	11A	27.6	
A-10e (51.8)	11A	24.7	
A-11a (0.0)	11A	24.1	
A-11b (29.9)	11A	26.4	
A-11c (56.4)	11A	25.6	
A-11d (57.0)	11A	25.9	
A-11e (90.5)	11A	26.2	
A-11f (122.8)	11A	26.5	
A-11g (84.1)	11A	27.5	
A-11h (51.8)	11A	28.5	
A-11i (24.4)	11A	26.1	
A-11j (0.0)	11A	25.1	
A-12a	11A	25.2	
A-11k	10	18.3	
A-12b	10	21.2	
A-13	10	19.9	
A-14	10	19.0	
A-15	6	8.5	
A-16	6	8.0	
A-17	6	4.2	
A-18a (0.0)	6	10.2	
A-18b (3.0)	6	9.2	19.1
A-18c (15.2)	6	9.5	19.0
A-18d (22.9)	6	8.3	
Lower Marble Samples			
A-33	Pierrepont	18.1	
A-34	Pierrepont	16.2	
A-35	Pierrepont	18.7	
A-36	Pierrepont	15.5	
A-37	Pierrepont	15.3	
A-38	Pierrepont	16.3	
A-39	Rossie	9.5	17.9
A-40	Russel	21.8	21.9
A-41	Russel	15.6	
A-42	N. Russel	18.1	19.3
A-43	N. Russel	16.9	
A-44	N. Russel	16.7	22.2
A-45	California	14.9	16.7
A-46	Pitcairn	11.7	

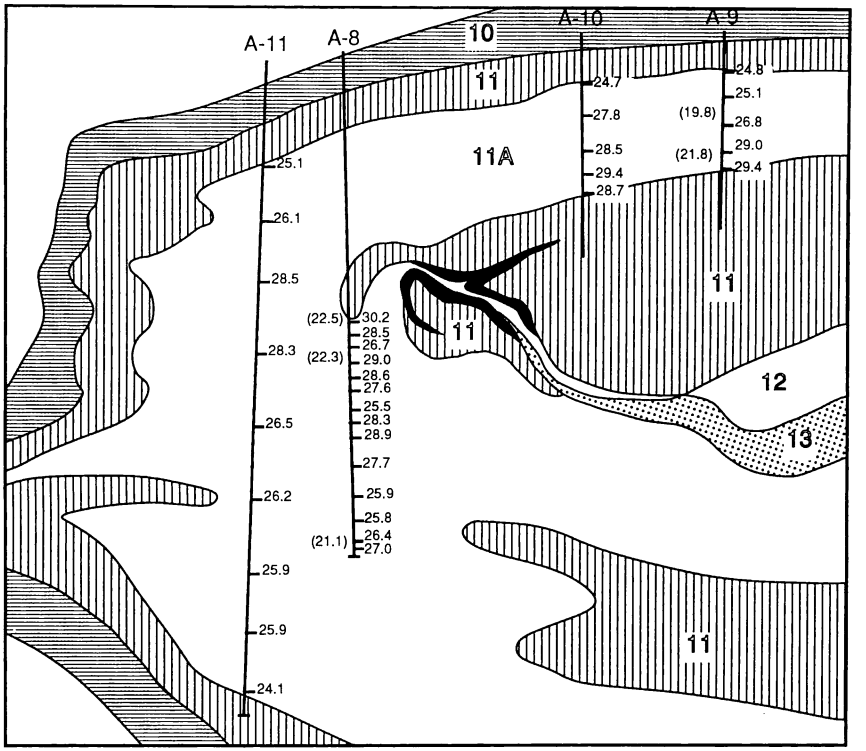


Fig. 3. Schematic cross section of the unit 11A anhydrite lens showing the variations of $\delta^{18}O_{anhy}$ values (in parentheses) and $\delta^{34}S_{anhy}$ values. The Fowler orebody (see fig. 2) is shown in black. Drill hole A-11 traversed approx 230 m of unit 11A. Drill hole numbers correspond to those in table 1.

The $\delta^{34}S$ values of non-ore pyrite from the Upper Marble increase abruptly in the middle part of unit 6 (fig. 4), from an average of −1.7 permil to an average of 7.8 permil. This increase coincides stratigraphically with the large increase of $\delta^{34}S_{anhy}$ values between unit 6 and units 10 and above, suggesting a coupling between the $\delta^{34}S_{anhy}$ and $\delta^{34}S_{sedpy}$ values. Possible explanations of this coupling are offered in the discussion section.

The $\delta^{34}S_{sedpy}$ values of the Pleasant Valley Gneiss, which is a possible lateral correlative of unit 2, average about −10 permil; significantly less than the $\delta^{34}S_{sedpy}$ values of unit 2, which average −2.8 permil.

$\delta^{18}O$ and $\delta^{13}C$ values of marble carbonate.—The $\delta^{13}C$ values ($\delta^{13}C_{carb}$) of Upper Marble carbonate range from −3.7 to 5.1 permil (table 3) with a bimodal distribution. The $\delta^{13}C_{carb}$ values of unit 6 (−3.7 to 0.7 permil) are distinctly lower than those of the rest of the Upper Marble (0.5−5.1 permil). The $\delta^{18}O$ values ($\delta^{18}O_{carb}$) of Upper Marble carbonate range from 22.6 to 26.6 permil (table 3).

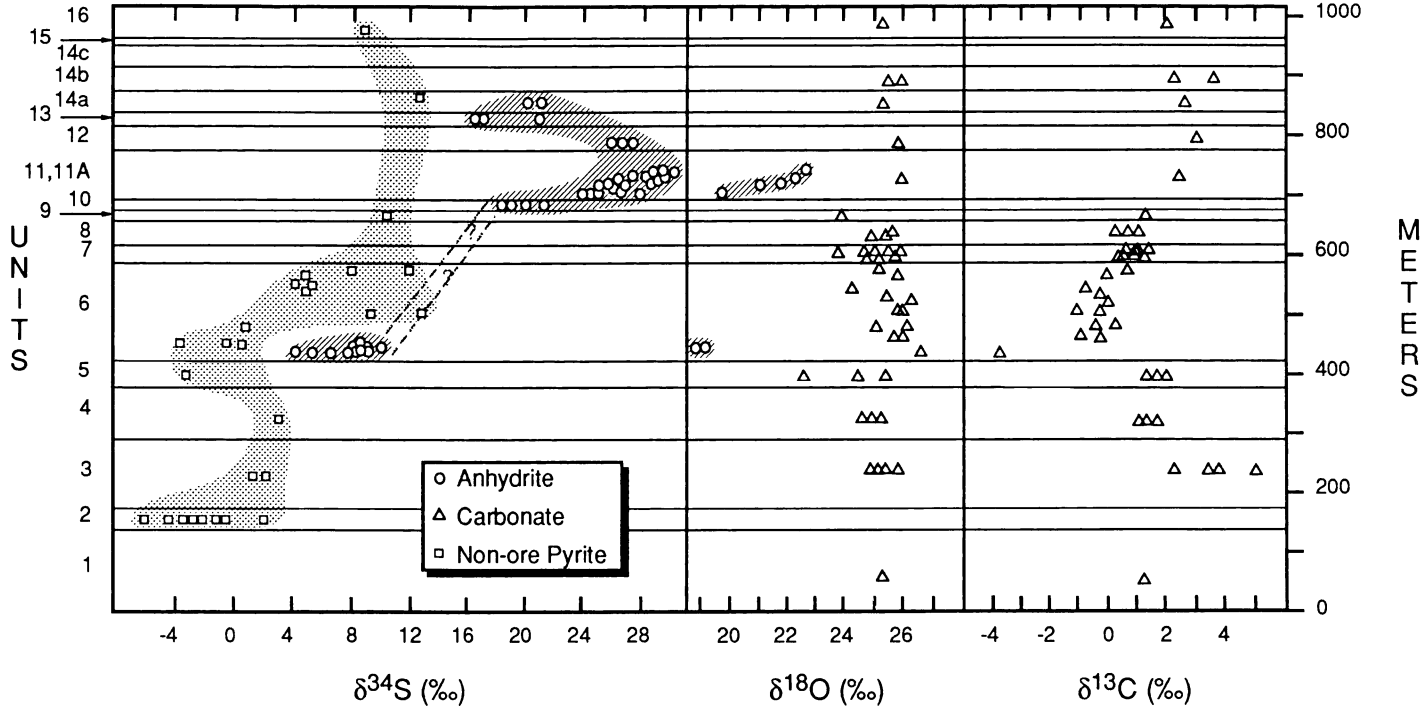


Fig. 4. The $\delta^{34}S$, $\delta^{18}O$, and $\delta^{13}C$ values of anhydrite, sulfide, and carbonate, with respect to stratigraphic position in the Upper Marble. Circles indicate anhydrite samples; squares indicate non-ore pyrite samples; and triangles indicate whole-rock carbonate samples. Sample position within units was determined from logs of cored drillholes.

TABLE 2

$\delta^{34}S$ values (permil) of sedimentary sulfides from the Upper Marble. Within each unit the samples are listed in approximate stratigraphic position from top to bottom

Sample No.	Unit	Mineral	$\delta^{34}S$(‰)
S-1	16	py	8.9
S-2	15	py	-17.5
S-3	14	py	12.7
S-4	9	py	10.5
S-5	6	py	12.0
S-6	6	py	8.0
S-7	6	py	3.0
S-8	6	sph	3.4
S-9	6	sph	2.2
S-10	6	py	3.1
S-11	6	py	12.9
S-12	6	py	9.5
S-13	6	py	0.8
S-14	6	py	-3.9
S-15	6	py	-3.7
S-16	6	py	0.6
S-17	6	py	-0.3
S-18	5	py	-4.2
S-19	4	sph	3.1
S-20	4	py	-31.6
S-21	3	py	1.4
S-22	3	py	2.2
S-23	2	py	1.9
S-24	2	py	-3.4
S-25	2	py	-1.0
S-26	2	py	-2.6
S-27	2	py	-1.6
S-28	2	py	-3.1
S-29	2	py	-4.6
S-30	2	py	-3.5
S-31	2	py	-6.5
S-32	Pleasant	py	-10.2
"	Valley	po	-10.2
S-34	Gneiss	py	-11.2
"	"	po	-11.3
S-35	"	po	-9.6

TABLE 3

$\delta^{13}C$ and $\delta^{18}O$ values (permil) of carbonates from the Upper Marble. Samples from units 6 and 7 are listed in their approximate stratigraphic position from top to bottom. Samples labelled "cc" are calcitic marbles, all the rest are dolomitic marbles

Sample No.	Unit	Mineral	$\delta^{13}C$(‰)	$\delta^{18}O$(‰)
C-1	16	cal	2.1	25.3
C-2	14	cal	3.7	25.5
C-3	14	dol	2.6	25.3
C-4	14	cal	2.3	25.8
C-5	12	dol	3.1	25.8
C-6	11	dol	2.6	25.9
C-7	9	cal	1.3	23.8
C-8	8	dol	0.9	25.3
C-9	8	dol	0.8	25.5
C-10	8	cal	0.5	24.9
C-11	7	dol	1.1	25.6
C-12	7	dol	0.9	25.0
C-13	7	dol	1.2	25.8
C-14	7	dol	1.3	25.9
C-15	7	dol	0.7	23.7
C-16	7	dol	0.7	25.3
C-17	7	dol	1.3	26.0
C-18	7	dol	0.5	24.6
C-19	7	dol	0.5	25.1
C-20	7	dol	1.0	25.7
C-21	7	dol	0.6	24.7
C-22	6	dol	0.7	25.1
C-23	6	dol	0.0	25.8
C-24	6	dol	-0.7	24.2
C-25	6	dol	-0.2	25.5
C-26	6	dol	0.0	26.2
C-27	6	dol	-1.0	25.9
C-28	6	dol	-0.2	26.0
C-29	6	dol	0.3	26.1
C-30	6	dol	-0.3	25.1
C-31	6	dol	-0.9	25.8
C-32	6	dol	-0.2	25.9
C-33	6	dol	-3.7	26.6
C-34	5	dol	1.5	22.6
C-35	5	dol	2.0	24.5
C-36	5	dol	1.6	25.4
C-37	4	dol	1.1	24.9
C-38	4	dol	1.4	24.6
C-39	4	dol	1.6	25.1
C-40	3	dol	3.5	25.4
C-41	3	dol	2.3	25.8
C-42	3	dol	5.1	25.2
C-43	3	dol	3.6	25.0
C-44	1	dol	1.2	25.3

The $\delta^{18}O_{carb}$ values of the Upper Marble are higher than those of other marbles of the Grenville Series. In a regional study of the Adirondack Lowlands that largely excluded the Balmat area, Valley and O'Neil (1984) reported dolomite $\delta^{18}O$ values ranging from 21.1 to 23.8 permil. The ^{18}O-enrichment and dolomitic composition of the Upper Marble are consistent with deposition or diagenesis in a hypersaline environment. The discussion section examines the possible significance of the coincidence of low $\delta^{13}C_{carb}$ values in unit 6 and the abrupt increase in $\delta^{34}S_{anhy}$ values between units 6 and 10.

$\delta^{18}O$ values of quartz—Oxygen isotope determinations of quartz were made in search of evidence for either a sandstone or chert protolith. The $\delta^{18}O$ values of quartz ($\delta^{18}O_{qz}$) from ten metaquartzite samples from unit 6 and one from unit 4 range from 25.3 to 27.9 permil (table 4). In less intensely metamorphosed rocks, these large values would clearly indicate a chert origin (Knauth and Lowe, 1978). The metaquartzites are, however, intensely recrystallized and, locally, criss-crossed with tiny fractures. Oxygen isotope exchange between quartz and other minerals in the sequence, mediated by the metamorphic pore fluid, must also be considered.

The isotopic composition of the metamorphic pore fluid would have been buffered by exchange with dolomite. Between 300° and 510°C, quartz has a $\delta^{18}O$ value slightly lower than that of dolomite (Northrop and Clayton, 1966; Clayton, O'Neil, and Mayeda, 1972). Assuming this relationship obtains at higher temperatures as well, the quartz in the metaquartzites is not in isotopic equilibrium with the dolomite. The average $\delta^{18}O_{qz}$ of unit 6 is 26.5 permil, which is almost 1 permil *larger* than the average $\delta^{18}O$ of the dolomite. This suggests the large $\delta^{18}O_{qz}$ values reflect a chert protolith. A chert protolith is also suggested by thin sections from four metaquartzite horizons that were stained for feldspar. None is present. Although pure quartz sandstones are known, minor contents of feldspar, as well as other easily identified

TABLE 4

$\delta^{18}O$ values (permil) of quartz from stratiform metaquartzites in the Upper Marble

Unit	$\delta^{18}O$
6	27.9
6	26.0
6	27.0
6	26.5
6	26.5
6	26.4
6	26.8
6	26.6
6	25.6
6	25.3
4	26.9

detrital components such as tourmaline and zircon, are much more common.

DEPOSITIONAL ENVIRONMENT OF THE ORIGINAL SEDIMENTS

The Upper Marble sequence formed either in a marine evaporitic setting or in a highly saline lacustrine basin. Distinguishing between marine and lacustrine depositional environments, however, is extremely difficult for Precambrian carbonate sediments, particularly when they have been highly metamorphosed.

Marine versus lacustrine deposition.—Criteria that distinguish marine and lacustrine settings were reviewed in detail by Kelts (1988). Textural and stratigraphic indicators (evidence of tidal influences, facies relationships, et cetera) have been obliterated from the Upper Marble by deformation and metamorphism. Fossil evidence is rare in the Precambrian, and land plants, which often label post-Devonian lacustrine carbonates with distinctly low $\delta^{13}C$ values (Keith and Weber, 1964), are absent. The isotopic composition and chemistry of lake water and lacustrine carbonate is controlled by the prevailing climate and the rock types being weathered in the drainage basins feeding the lake. Some geochemical indicators present in the Upper Marble ($\delta^{13}C_{carb}$ values near 0 permil; $\delta^{18}O_{carb}$ values $\geq$25 permil; $\delta^{34}S_{anhy}$ values $\geq$20 permil; presence of halite; et cetera) may suggest a marine setting. Such indicators are, however, always equivocal in that mineralogical and geochemical relationships *typical* of marine deposition can always have formed in an *atypical* lacustrine environment. Moreover, marine evaporites generally form in highly continental environments, further clouding distinctions between marine and lacustrine settings.

Although there is no conclusive evidence of either a marine or lacustrine setting of the Upper and Lower Marbles, all preserved evidence supports a marine carbonate setting. Features of the Upper Marble suggestive of marine deposition are:

1. The thick and laterally extensive, clastic-poor nature of the Grenville Series carbonates.
2. Upper Marble carbonates have $\delta^{13}C$ values close to 0 permil and $\delta^{18}O$ values generally >25 permil, and the Lower Marble carbonate is similar with slightly lower $\delta^{18}O$ values, typical of marine carbonate. The ^{18}O-enrichment of the Upper Marble suggests deposition from or diagenesis by highly evaporated seawater.
3. The $^{87}Sr/^{86}Sr$ ratios of Upper Marble carbonate and anhydrite (Hoff, ms; Hoff, Grant, and Whelan, 1984) resemble those of mid-Proterozoic seawater (Veizer and Compston, 1976). The $^{87}Sr/^{86}Sr$ ratios of lacustrine carbonates are typically more radiogenic than marine carbonates because of increased input from older continental crust.
4. Tourmaline from unit 13 has $\delta^{11}B$ values of 6.7 permil (Palmer and Slack, in press) and 12 permil (Swihart and Moore, 1989).

Palmer and Slack (in press) conclude that these boron isotopic compositions indicate a marine boron source.

5. The sulfur isotope geochemistry of the anhydrite strongly suggests input of oceanic sulfate. Most of the anhydrite in the Upper Marble has $\delta^{34}S$ values >15 permil, typical of marine evaporites (Claypool and others, 1980), whereas lacustrine dissolved sulfate $\delta^{34}S$ values range between 3 and 17 permil (studies cited by Nielsen, 1978).

Anhydrite deposition-evaporitic or hydrothermal?—Bedded anhydrite can form in both syngenetic hydrothermal and sedimentary evaporitic settings. There are several compelling arguments for an evaporitic origin. The anhydrite horizons in the Upper Marble are of considerable lateral extent. Bedded anhydrite has been encountered throughout the Upper Marble, from Balmat to Edwards, a distance of 15 km (fig. 1). The anhydrite can be thick, unit 11A exceeds 40 m in its thinnest portions, and is tabular. Lastly, the anhydrite occurs, in general, independent of the massive sulfide orebodies. (Anhydrite from unit 11A is associated with the Fowler orebody, but deLorraine (ms) and deLorraine and Dill (1982) attribute that to plastic injection of anhydrite along a ruptured thrust fault.)

Sabkha or subaqueous?—Evaporites may form subaqueously, in shallow or deep water, or subaerially, in sabkha (supratidal) settings. We think that the Upper Marble evaporites are subaqueous. Again, however, no conclusive sedimentologic or petrologic evidence distinguishing between sabkha and subaqueous settings has survived the metamorphism of the Upper Marble.

Sabkha sequences display rapid facies changes, commonly with lenses of terrigenous detritus (Schreiber, 1978; Handford, 1981), whereas the units of the Upper Marble are sheetlike and persistent (Brown and Engel, 1956; deLorraine, in preparation). Sabkha anhydrite can be volumetrically minor and often occurs primarily as interstitial cements and nodular horizons (Kendal, 1984), whereas Upper Marble anhydrite occurs as thick layers of nearly pure anhydrite. Continental sediments, such as eolian quartzites or redbeds, are common in sabkha sequences (Schreiber, 1978); such sediments have yet to be recognized in the Grenville Series of the Adirondack Lowlands. Furthermore, metaquartzites in the Upper Marble are thinly layered to laminated and show no evidence of shallow-water, tidal-influenced deposition such as crossbedding, ripple-bedding, or rip-up breccias.

It is unfortunate and frustrating that the sedimentational setting of the Upper Marble and the important Zn-Pb ores it hosts cannot be tightly constrained. Fortunately, many of the conclusions suggested by our geochemical studies are independent of the depositional setting of the evaporites, be it marine or lacustrine, supratidal or subaqueous.

ISOTOPE GEOCHEMISTRY OF UPPER MARBLE ANHYDRITE

The anhydrite lenses of the Upper Marble are unusual, perhaps unique, in three respects: (1) $\delta^{34}S_{anhy}$ values range from 4.2 to 30.2

permil, a range greater than that measured in any other evaporite sequence; greater, in fact, than the entire range displayed by Phanerozoic marine evaporites (Claypool and others, 1980). (2) The $\delta^{34}S_{anhy}$ values of unit 6 are lower than any post-Archean marine evaporites and distinctly lower than the rest of the Upper Marble anhydrite. (3) Both $\delta^{34}S_{anhy}$ and $\delta^{18}O_{anhy}$ values increase upsection in unit 11A. Coupled increases of sulfate $\delta^{34}S$ and $\delta^{18}O$ values are a predicted consequence of bacterial sulfate reduction in a closed system (Claypool and others, 1980). As far as we are aware, however, this is the first reported preservation of this covariance in an evaporite sequence.

A brief review of the isotope geochemistry of marine sulfate.—Secular variations of the $\delta^{34}S$ value of seawater sulfate, as preserved by marine sulfate evaporites, are known to at least 1200 Ma, with a general range between 10 and 30 permil (this paper; Claypool and others, 1980). Present-day seawater sulfate has a $\delta^{34}S$ value near 20 permil (Sasaki, 1972).

The estimated $\delta^{34}S$ value of sulfate added to the ocean by weathering is probably near 0 permil (Claypool and others, 1980). The sulfate content of freshwaters is generally low, however, typically in the $\mu g/kg$ range, much less than the sulfate content of seawater, which is 2712 mg/kg (Holland, 1978). The decrease of $\delta^{34}S$ value of marine sulfate caused by continental runoff will, therefore, be slow. Sulfate is removed from seawater directly by precipitation of evaporitic and authigenic sulfate minerals and indirectly by reduction and precipitation of sulfide minerals. Calcium sulfate precipitated from seawater is enriched in ^{34}S by 1.65 permil (Thode and Monster, 1965) and in ^{18}O by $\approx$3.6 permil (Holser and others, 1979) with respect to the dissolved sulfate.

Anaerobic sulfate-reducing bacteria utilize sulfate oxygen in the metabolization of organic matter, with CO_2 and H_2S waste products. Sulfate-reducing bacteria preferentially metabolize isotopically light sulfate, thereby enriching the residual sulfate in the heavier isotopes. This reduction is simply generalized as

$$2(CH_2O) + SO_4^{-2} \xrightarrow{\text{bacteria}} 2HCO_3^- + H_2S. \quad (1)$$

In natural environments, the $\delta^{34}S$ value of the product H_2S is typically 40 to 60 permil less than that of the reactant sulfate (Kaplan, Emery, and Rittenberg, 1963; Goldhaber and Kaplan, 1974, 1975, and 1980). If this H_2S is removed, by precipitation as metal (typically Fe) sulfide or reaction with organic matter, the residual sulfate will be enriched in ^{34}S. Otherwise, the H_2S will eventually reoxidize and the sulfate $\delta^{34}S$ values will be unchanged. Sulfate $\delta^{18}O$ values also increase during bacterial sulfate reduction, but only one-half to one-quarter as much as the $\delta^{34}S$ values; that is, if the $\delta^{34}S$ value increases by 10 permil the $\delta^{18}O$ value should increase by 2.5 to 5 permil (Holser and others, 1979; Zak, Sakai, and Kaplan, 1980).

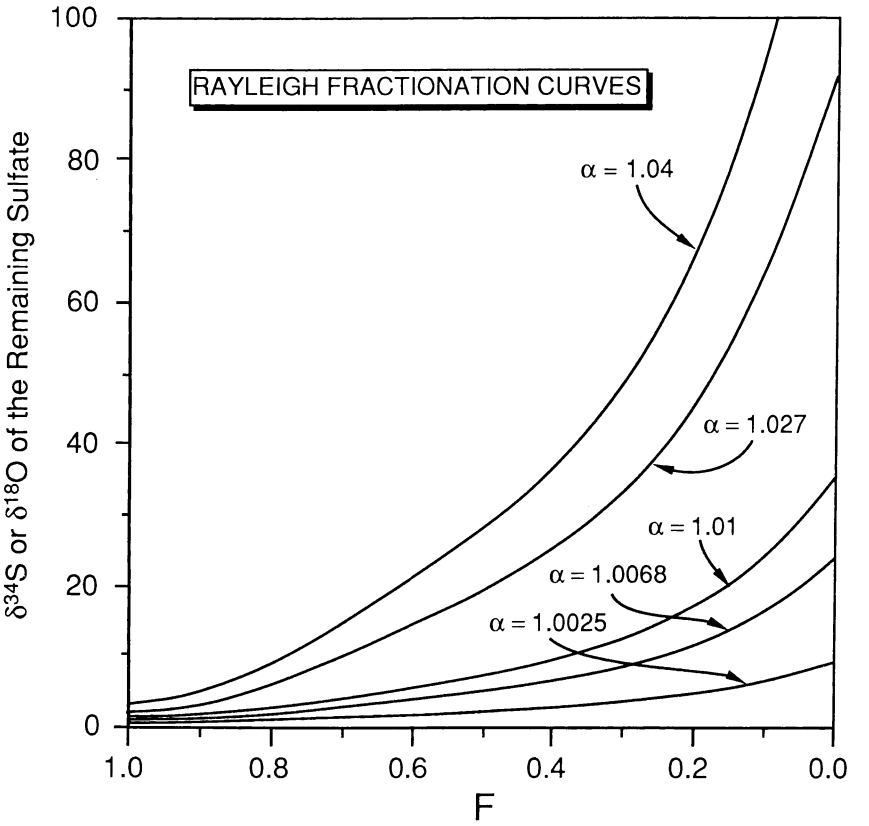


Fig. 5. Rayleigh fractionation curves for different values of α. F is the fraction of sulfate remaining. For sulfur, α is the kinetic isotopic fractionation between the remaining sulfate and the product H_2S; for oxygen, α is the kinetic isotopic fractionation between the remaining sulfate and the products of reaction 1.

The increases in the $\delta^{34}S$ and the $\delta^{18}O$ values of the anhydrite in the Upper Marble are easily modelled by bacterial reduction of sulfate in a closed basin; that is, Rayleigh distillation. Figure 5 shows the increases in the $\delta^{34}S$ or $\delta^{18}O$ value of the sulfate at different values of α[1], the fractionation factor between residual and metabolized sulfate. Even at comparatively modest α's of $\approx$1.027 for S and $\approx$1.0025 for O, bacterial sulfate reduction readily produces increases in the $\delta^{34}S$ and $\delta^{18}O$ values of the sulfate comparable to that within unit 11A and that between unit 6 and the younger anhydrite lenses of the Upper Marble (fig. 5). The

[1] The isotopic fractionation factor between two phases, $\alpha_{A\text{-}B}$, equals $(1 + \delta_A/1000)/(1 + \delta_B/1000)$, or $1000 + \delta_A/1000 + \delta_B$. An α of 1.025 indicates that phase A is enriched by $\approx$25 permil with respect to phase B.

clear positive correlation between the $\delta^{34}S_{anhy}$ and $\delta^{18}O_{anhy}$ of unit 11A is also consistent with a Rayleigh fractionation model.

A closed basin cannot, however, account for the large quantities of anhydrite preserved in the Upper Marble. Complete evaporation of a column of seawater 1 km deep results in the deposition of only 0.53 m of calcium sulfate (Holser, 1979), far less than the 40 m minimum thickness of anhydrite in unit 11A. Therefore, although concurrent bacterial sulfate reduction and evaporite formation are indicated at Balmat, it is unlikely that the Upper Marble depositional basin was closed. Deposition of significant thicknesses of evaporite minerals requires periodic input of dissolved salts.

Non-ore pyrite in the Upper Marble.—The origin of the pyrite in the pyritic graphitic schists and that that occurs in trace amounts in most of the Upper Marble units is uncertain. The $\delta^{34}S$ values of ore pyrite are much larger than those of the non-ore pyrite, ranging from 13 to 17.5 permil, and are independent of stratigraphic position (Whelan, Rye, and deLorraine, 1984). Furthermore, the orebody pyrite contains much less nickel and cobalt than the non-ore pyrite (Doe, 1962). It is unlikely, therefore, that the non-ore pyrite has a hydrothermal origin.

The interpolated $\delta^{34}S$ variations of the non-ore pyrite do, however, appear to track those of the anhydrite, but offset to values about 10 permil less than that of the anhydrite (fig. 4). Interdependence of non-ore pyrite and anhydrite $\delta^{34}S$ values could reflect deposition, diagenesis, or metamorphism.

Pyrite in black shales and carbonate sedimentary rocks is often of biogenic origin, arising from the bacterial reduction of sulfate during deposition or diagenesis. The $\delta^{34}S$ values of the non-ore pyrite in the Upper Marble do not fit neatly into this mold. At a $\delta^{34}S$ decrease of 40 to 60 permil, typical of seafloor bacterial reduction, biogenic pyrite in the Upper Marble should range from -10 to -50 permil. Only the non-ore pyrite from the Pleasant Valley Gneiss is within this range, the rest generally has much higher $\delta^{34}S$ values. Increase in the rate of bacterial sulfate reduction, due to optimal temperatures or increased nutrient availability, decreases the fractionation during reduction and produces pyrite with higher $\delta^{34}S$ values. Increased rates could, thus, account for the higher $\delta^{34}S_{sedpy}$ values and, if the rates were nearly constant, for the comparatively constant difference between the $\delta^{34}S_{sedpy}$ and $\delta^{34}S_{anhy}$ values.

A limited supply of sulfate during diagenesis allows more quantitative sulfate reduction and larger $\delta^{34}S$ values in the resulting pyrite. Moreover, thermochemical reduction of the sulfate by reaction with organic compounds at temperatures of 70° to 120°C (Orr, 1977) often results in diagenetic pyrite with $\delta^{34}S$ values about 15 permil less than the reactant sulfate. Either of these processes could account for the range and variations of the $\delta^{34}S_{sedpy}$ values.

Whelan, Rye, and deLorraine (1984) reported a consistent difference of 9 to 10 permil between the $\delta^{34}S$ values of intimately coexisting

pyrite and anhydrite in ore or country rock that apparently reflects isotopic equilibration at 600° to 650°C during metamorphism (Whelan, Rye, and deLorraine, 1984). This 9 to 10 permil difference is similar to the inferred difference between stratigraphically correlative pyrite and anhydrite, suggesting that metamorphic equilibration might also account for the latter systematics. This intriguing possibility requires sulfur isotope exchange between non-ore pyrite and anhydrite over large distances. Such exchange, if it occurred, must have been mediated by the metamorphic pore fluid.

Chemical events.—Large and rapid increases in the $\delta^{34}S$ values of seawater sulfate are recorded by evaporite sequences in the Cambrian of the Soviet Union, the Devonian of the Province of Saskatchewan, Canada, and the Triassic of northern Europe (fig. 6). These increases and the processes that caused them were christened "chemical events" by Holser (1977).

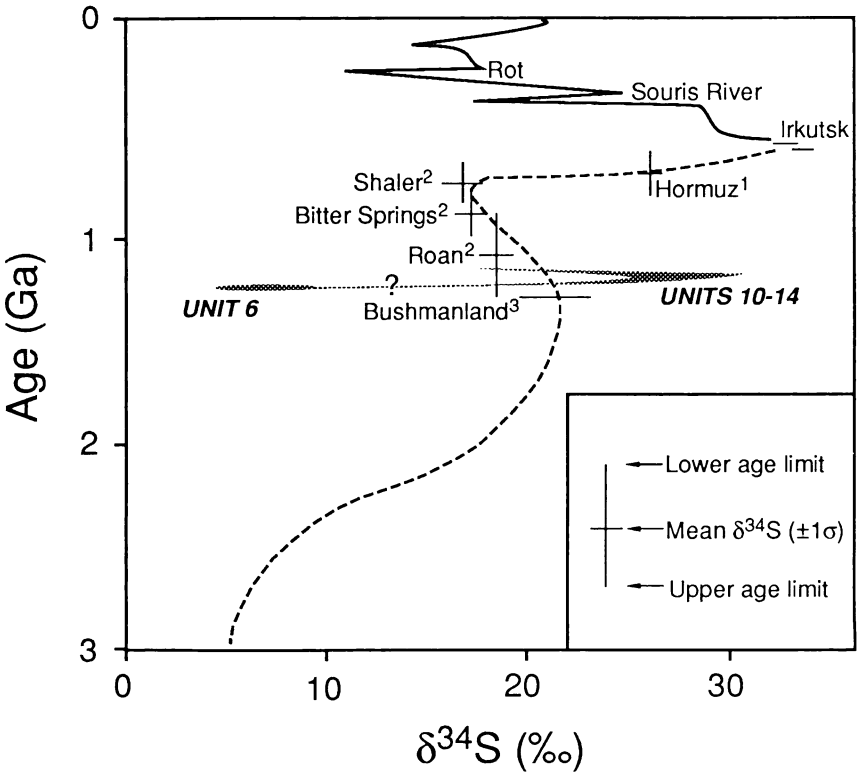


Fig. 6. The secular variations of the $\delta^{34}S$ value of seawater sulfate. Irkutsk, Souris River, and Röt chemical events are plotted from Holser (1977). Data from this paper, [1]Houghton (ms), [2]Claypool and others (1980), and [3]Holser and others (1988).

Chemical events are signalled by: (1) a large, worldwide increase in the $\delta^{34}S$ value of seawater sulfate that may be punctuated by (2) extreme increases in the $\delta^{34}S$ values of sulfate in one or more evaporite basins, labelled "positive overshoots." The increase is followed by (3) a long period during which the $\delta^{34}S$ values of seawater sulfate gradually wane to more normal values. Where "positive overshoots" are recorded, they are confined to a narrow stratigraphic interval, indicating that, (4) the $\delta^{34}S$ increase was geologically abrupt. Finally, (5) the $\delta^{18}O$ values of the sulfate evaporites in the overshoot basins do not track the $\delta^{34}S$ increase but remain at their pre-overshoot value (Holser, 1977).

Holser (1977) proposed that chemical events record the sudden addition of a large quantity of sulfate-rich, ^{34}S-enriched brine to the ocean, producing a transient maxima in seawater sulfate $\delta^{34}S$ values. Restoration of pre-event $\delta^{34}S$ values might take tens of millions of years. Where evaporite deposition sampled the brine before it lost its identity by mixing with the ocean, a "positive overshoot" was recorded. Holser (1977) suggested that chemical event brines originated in large basins that were not in open communication with the ocean. Schmalz (1969) suggested that evaporites could accumulate in the bottoms of deep, barred basins.

Brine formation results through evaporation of seawater at the basin surface. As evaporation proceeds, the denser brine settles in the bottom of the basin, stagnates and becomes anoxic, and is an ideal site for bacterial sulfate reduction. With time, such a brine might become highly saline and extremely ^{34}S-enriched. Mixing of such a brine into the ocean, through tectonism or overturn, is the chemical event of Holser (1977). Marine evaporites forming outside the basin at that time would record the event as an abrupt increase of $\delta^{34}S$ values.

The isotope systematics of evaporites formed within the basin of brine accumulation would, however, differ significantly from those of evaporites formed outside the basin. Extra-basin evaporites would record a sudden increase of $\delta^{34}S$ values followed by a gradual decrease as the brine mixed with the ocean. Evaporites formed within the basin during brine accumulation would record a gradual increase of $\delta^{34}S$ values followed by an abrupt decrease when seawater mixed with the basin water. Heretofore, only indirect evidence of a "chemical event" brine has been recorded. We believe the Upper Marble records the presence of a brine—that is, that the Upper Marble depositional basin was a "holding tank" where a sulfate-rich, ^{34}S-enriched brine accumulated.

Balmat—a brine basin?—Several aspects of the Upper Marble data are consistent with deposition in a brine "holding tank."

(1) The smooth, continuous increases of anhydrite $\delta^{34}S$ and $\delta^{18}O$ values during the deposition of unit 11A are compatible with concurrent anhydrite deposition and bacterial sulfate reduction in a stagnant, highly saline brine. Furthermore, the $\delta^{34}S_{anhy}$ values increased about twice as much as the $\delta^{18}O_{anhy}$ values, in good agreement with both field

and laboratory measurements of the heavy-isotope enrichment of sulfate that accompanies bacterial reduction (Holser, 1979).

(2) Biogenic H_2S must be removed for brine sulfate $\delta^{34}S$ and $\delta^{18}O$ values to increase. If the biogenic H_2S remains in the euxinic brine, it will quickly reach concentrations toxic to the sulfate reducing bacteria (Berner, 1985). If it returns to the surface environment, it will oxidize and rejoin the sulfate reservoir. Either course will retard heavy-isotope enrichment of the brine sulfate. Only removal of the H_2S, by formation of pyrite or, perhaps, organosulfur compounds, can result in large increases of the brine sulfate $\delta^{34}S$ values. A "holding tank" basin must, therefore, also contain reduced-sulfur-rich sediments.

The Upper and Lower Marbles and the Popple Hill Gneiss contain pyritic graphitic zones (fig. 1), the metamorphic equivalents of pyritic organic-rich sediments (Buddington, Jensen, and Mauger, 1969). The $\delta^{34}S$ values of these sulfides are quite variable and generally less than -10 permil, common aspects of sulfides formed from biogenic H_2S (Buddington, Jensen, and Mauger, 1969). Presently, no pyritic facies is known that is stratigraphically equivalent to the anhydrite-bearing part of the Upper Marble. Lateral correlations are extremely difficult, however, because of the complex structure and possible unrecognized facies changes. The recurrence of "biogenic"-pyrite-rich facies in the marbles does, however, indicate that the anoxic bottom conditions conducive to large-scale bacterial sulfate reduction were commonplace.

(3) The $\delta^{13}C_{carb}$ values of unit 6 are the lowest in the Upper Marble (fig. 4). The reduced carbon content and $\delta^{18}O_{carb}$ values of unit 6 are similar to the other marbles. The lower $\delta^{13}C$ values are, therefore, unlikely to reflect either diagenetic or metamorphic changes. Bacterial reduction of sulfate, however, oxidizes two moles of organic carbon for every mole of sulfate reduced (reaction 1), producing HCO_3^- with $\delta^{13}C$ values of -25 to -30 permil (Degens, 1969). Perhaps bacterial reduction of sulfate contributed enough ^{13}C-depleted HCO_3^- to the basin to lower the $\delta^{13}C_{carb}$ values of unit 6.

(4) The occurrence of evaporites and the general ^{18}O-enrichment of Upper Marble carbonates indicate an arid climate, a precondition for a brine-accumulating basin.

We believe that the Upper Marble precursors were deposited in a holding-tank basin. The record of marine evaporite $\delta^{34}S$ variations during the Proterozoic, however, is too incomplete to provide corroborating evidence of a chemical event. Furthermore, the size of the Upper Marble basin is unknown and hence the volume of brine it might have contained. A basin based on the present outcrop of the Upper Marble could not hold enough brine to increase significantly the isotopic composition of the world's oceans.

Unit 6.—Claypool and others (1980) estimated that the $\delta^{34}S$ value of mid-Proterozoic seawater sulfate averaged ≈ 17 permil. The average $\delta^{34}S_{anhy}$ value of unit 6 is 8 permil, not only considerably lower than this estimate, but lower than any other marine evaporite (Holser and

Kaplan, 1966; Claypool and others, 1980). Furthermore, there is no other evidence of marine evaporites with such low $\delta^{34}S$ values in the Proterozoic (Holser and others, 1988). Large variations from the norm, as in the Upper Marble, would be easier to produce in the smaller volume of a lacustrine basin. Furthermore, the lower $\delta^{34}S_{anhy}$ values in unit 6 are suggestive of continent-derived freshwater sulfate. Enormous quantities of freshwater, however, would be required to lower the $\delta^{34}S$ values to 8 permil, and neither the large $\delta^{18}O_{carb}$ values of unit 6 nor the deposition of evaporites in unit 6 are compatible with a large freshwater influx.

Bacterial sulfate reduction caused increases in the $\delta^{34}S_{anhy}$ and $\delta^{18}O_{anhy}$ values. It may also have caused the low $\delta^{34}S_{anhy}$ values of unit 6. Figure 7 is based on the deep-water evaporite model of Schmalz (1969) and the chemical-event brine basin of Holser (1977). The basin bathymetry is simplified and evaporite deposition is placed in close proximity to the site of bacterial sulfate reduction, when, in reality, they could be widely separated.

Figure 7A shows the basin at the beginning of brine accumulation. Evaporation produces brines along the basin margins which settle in the basin deeps. Anoxia and bacterial sulfate reduction lead to the deposition of biogenic sulfides and ^{34}S-enrichment of the residual sulfate in the brine. Evaporitic calcium sulfate may deposit in coastal sabkhas, on shallow shelfs, or, if brine salinity permits, in the basin deeps. Sabkha and shelf anhydrite will reflect the $\delta^{34}S$ of the surface waters; that in the deeps, the brine.

Figure 7B shows some of the sulfur geochemistry of a basin during brine accumulation. Pyrite formation removes some of the H_2S. Inevitably, however, some H_2S (much of it, if iron availability is low) will escape, rise in the water column, and oxidize. Significantly, hydrothermal ores in the Upper Marble are all younger than the unit 6 anhydrite (deLorraine and Dill, 1982).

Oxidation of H_2S will add sulfate with very low ($\ll$0 permil) $\delta^{34}S$ values to the surface waters. Extensive oxidation of H_2S in the surface waters could lead to deposits of ^{34}S-depleted evaporitic sulfate in sabkha or shelf settings, while in the deeps of the basin, a ^{34}S- enriched, sulfate-rich brine accumulates.

The $\delta^{18}O_{anhy}$ values in the Upper Marble, higher than most marine evaporites (Claypool and others, 1980), may support wholesale H_2S oxidation. Lloyd (1968) determined that oxidation of H_2S in seawater utilizes molecular oxygen from H_2O and dissolved oxygen in a ratio of $\approx$2:1 and derived the following equation to predict the $\delta^{18}O$ value of the resulting sulfate:

$$\delta^{18}O = X(\delta_w + \epsilon_w) + (1 - X)(\delta_a + \epsilon_a). \quad (2)$$

In eq (2), X is the proportion of oxygen from water molecules, δ_w and δ_a are the respective $\delta^{18}O$ values of seawater and the oxygen dissolved in it,

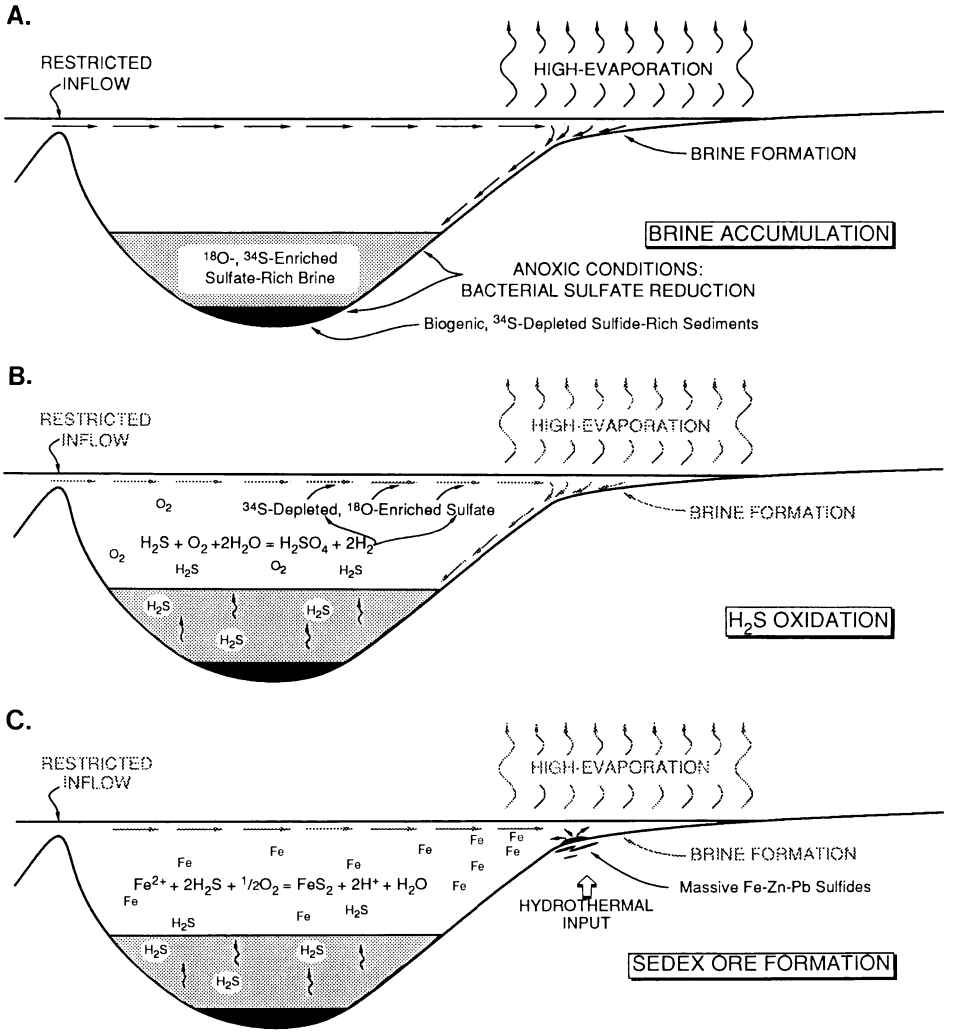


Fig. 7. A hypothetical restricted basin as proposed by Schmalz (1969) and Holser (1977) for brine accumulation and evaporite deposition. In (A), evaporation of seawater in the shelf and tidal zones forms concentrated brines which pond in the bottom of the basin. The paths of inflowing seawater and sinking brine are indicated by arrows. Stagnation of the ponded brine promotes bacterial sulfate reduction, resulting in ^{34}S- and ^{18}O-enrichment of the residual sulfate. Organic-matter-rich, possibly sulfide-rich, sediments accumulate beneath the brine; (B) shows the possible movement of sulfur between oxidized surface waters and reduced bottom waters during deposition of unit 6 anhydrite. Biogenic H_2S production has exceeded the supply of metals for sulfide formation, and the excess H_2S has risen in the water column and been oxidized to sulfate. This oxidation, in effect, distills ^{32}S from the basin brine and into the overlying surface waters. The isotopic compositions of evaporites formed from these surface waters would not necessarily reflect either seawater or the basin brine; (C) possible increase in the iron concentration of the basin waters during synsedimentary hydrothermal activity.

and ϵ_w and ϵ_a are the respective oxygen isotopic fractionations between seawater and the product sulfate and between dissolved oxygen and the product sulfate.

Holser and others (1979) assumed values of X = 0.68, δ_w = 0 permil, ϵ_w = 0 permil, δ_a = 28 permil, and ϵ_a = −8.7 permil, and calculated that sulfate from H_2S oxidation should have a $\delta^{18}O$ value of 16.2 permil. Calcium sulfate precipitated from seawater with this sulfate would have a $\delta^{18}O$ value of 19.8 permil, quite similar to the $\delta^{18}O_{anhy}$ values of unit 6 and at the base of unit 11A.

Freshwater influx and calcium sulfate precipitation *decrease* the $\delta^{34}S$ and $\delta^{18}O$ values of marine sulfate. Bacterial reduction of sulfate *increases* the $\delta^{34}S$ and $\delta^{18}O$ values of marine sulfate (Claypool and others, 1980). Only sulfide oxidation can increase $\delta^{18}O_{anhy}$ values while decreasing $\delta^{34}S_{anhy}$ values and is, therefore, consistent with both the low $\delta^{34}S_{anhy}$ values of unit 6 and the high $\delta^{18}O_{anhy}$ values of units 6 and 11A. Some H_2S probably always escapes precipitation during bacterial reduction of sulfate. The very low $\delta^{34}S_{anhy}$ values of unit 6 suggest, based on this scenario, extensive cycling of H_2S between the brine and surface reservoirs.

The upsection increase of $\delta^{34}S_{anhy}$ values in unit 11A implies that anhydrite precipitation was concurrent with large-scale bacterial sulfate reduction. Unit 11A, therefore, was deposited either (1) subaqueously, in the brine pool *a la* the model of Schmalz (1969); (2) after the brine completely filled the basin; or, (3) when the basin was completely isolated and overturn or diffusion mixed the ^{34}S-enriched brine sulfate with the overlying waters.

Impact of synsedimentary ore formation.—The increases in the $\delta^{34}S$ values of marine sulfate recorded by chemical events require enormous deposits of ^{34}S-depleted biogenic iron sulfide elsewhere in the "holding tank" basin. Iron is delivered to the seas largely in the sediment load of rivers (Berner, 1985) or by submarine springs. The sparse clastic content of the Upper Marble protolith and the evidence of arid and saline conditions argue that riverine input to the depositional basin was minimal. Furthermore, the extremely high iron content of some of the pyritic schists (>70 wt percent) would seem to exceed the capacity of a sediment clay fraction to provide iron. The synsedimentary massive sulfide (sedex) deposits in units 6 through 14, however, indicate that submarine hydrothermal activity was roughly coincident with the increase of $\delta^{34}S_{anhy}$ values. Whelan, Rye, and deLorraine (1984) concluded that, although the sulfur in the Zn-Pb orebodies had an origin similar to that in MVT fluids, the sedex fluids may have been an important source of iron to the Upper Marble depositional basin.

Submarine hydrothermal solutions discharging into the Gulf of California are analogous to the setting at Balmat in that they pass through a pile of marine sediments before reaching the seafloor (Von Damm and others, 1985). The iron content of these high-temperature solutions ranges from ≈1 to ≈10 mg/kg of solution. This contrasts

strongly with the typical iron contents of seawater, ≈0.002 mg/kg, and freshwater, ≈0.5 mg/kg (Holland, 1978). Submarine hot springs in closed or restricted basins must be an important (the dominant?) source of iron. As in the Atlantis II deep of the Red Sea, this iron would be precipitated quickly as oxides, hydroxides, or sulfides and settle to the floor of the basin (Bischoff, 1969).

Balmat is not the only sedex deposit where the $\delta^{34}S$ values of sulfate in the basin apparently increased during hydrothermal episodes. At McArthur River, Australia (Smith and Croxford, 1973; Williams and Rye, 1974) and Outokumpo, Finland (Makela, 1974), the $\delta^{34}S$ values of non-ore pyrite increased during the formation of the ores. These non-ore pyrite $\delta^{34}S$ values probably track similar increases in the $\delta^{34}S$ of the sulfate available for bacterial reduction and may be, by analogy, evidence of ore deposition in a restricted basin of brine accumulation. The McArthur River sequence also contains evidence of evaporite deposition (Walker and others, 1977).

Synsedimentary ore deposition and evidence of restricted basin brine accumulation coincide in the Upper Marble. This suggests that sedex hydrothermal activity, as an iron source, may be an important factor in the ^{34}S-enrichment of the brine sulfate, one that should be added to Holser's (1977) model of a chemical event basin. The geologic record is replete with examples of pyrite-rich black shales which had no demonstrable effect on the $\delta^{34}S$ of marine sulfate. Iron input from submarine hydrothermal activity may be required to fix more efficiently the product H_2S and promote ^{34}S-enrichment of the brine sulfate (Whelan, Rye, and deLorraine, 1984). Furthermore, sedex deposits such as Balmat, McArthur River, and the Red Sea (Shanks and Bischoff, 1980) are frequently associated with proto-rift or fault-bounded continental basins. Not only are such basins frequent sites of hydrothermal activity, they are often isolated from the ocean and provide suitable conditions for the formation of marine evaporites (Kinsman, 1975).

Chemical events do not require hydrothermal activity. Given long periods of tectonic stability, any restricted basin could accumulate a ^{34}S-enriched, sulfate-rich brine, with normal inputs of iron. Hydrothermal activity, however, can amplify and (or) accelerate the increase in the $\delta^{34}S$ of the brine sulfate by providing metals (primarily iron) for the extraction of bacterially-produced H_2S. Hydrothermal fluids might also (1) contribute to the formation of dense, stagnant brines, as in the Atlantis II Deep of the Red Sea; and (2) due to the retrograde solubility of anhydrite (Holland, 1979), promote anhydrite precipitation by warming of the basin water.

SUMMARY

1. The presence of anhydrite and the stable isotopic composition of carbonate in the Upper Marble record an arid climate.

2. The existence of large deposits of biogenic–sulfide–rich metasediments, of a $\delta^{13}C_{carb}$ decrease in unit 6, and of positively correlated

increases in both the $\delta^{34}S$ and $\delta^{18}O$ values of the anhydrite in unit 11A imply that the Upper Marble anhydrite lenses were deposited in a restricted basin that was the site of accumulation of highly saline brines and extensive bacterial sulfate reduction. This basin is analogous to the basins Holser (1977) hypothesized must have sourced brines responsible for chemical events.

3. The low $\delta^{34}S$ and high $\delta^{18}O$ values of the anhydrite in unit 6 may record oxidation of biogenic H_2S in the surface waters of the depositional basin.

4. Estimations of iron availability during bacterial sulfate reduction suggest that the synsedimentary hydrothermal activity that produced the large sedex deposits in the Upper Marble may have been a contributing factor in the ^{34}S-enrichment of the brine sulfate by providing a source of iron for the precipitation of bacterially-generated H_2S.

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REFERENCES

Bailey, S. A., and Smith, J. W., 1972, Improved method for the preparation of sulfur dioxide from barium sulfate for isotope ratio studies: Analytical Chemistry, v. 44, p. 1542–1543.

Barton, J. M., and Doig, R., 1974, Temporal relationships of rock units in the Shawinigan area, Grenville Province, Quebec: Canadian Journal of Earth Science, v. 11, p. 686–690.

Berner, R. A., 1985, Sulphate reduction, organic matter oxidation, and pyrite formation: Philosophical Transactions of the Royal Society of London, v. 315, p. 25–38.

Bischoff, J. L., 1969, Red Sea geothermal brine deposits: their mineralogy, chemistry, and genesis, *in* Degens, E. T., and Ross, D. A., eds., Hot Brines and Recent Heavy Metal Deposits in the Red Sea: New York, Springer-Verlag, p. 368–401.

Bohlen, S. R., and Essene, E. J., 1977, Feldspar and oxide thermometry of granulites in the Adirondack highlands: Contributions to Mineralogy and Petrology, v. 62, p. 153–169.

Brown, J. S., 1973, Sulfur isotopes of Precambrian sulfates and sulfides in the Grenville of New York and Ontario: Economic Geology, v. 68, p. 362–370.

Brown, J. S., and Engel, A. E. J., 1956, Revision of Grenville stratigraphy and structure in the Balmat-Edwards district, northwest Adirondacks, N.Y.: Geological Society of America Bulletin, v. 67, p. 1599–1622.

Brown, P. E., Essene, E. J., and Kelly, W. C., 1978, Sphalerite geobarometry in the Balmat-Edwards district, New York: American Mineralogist, v. 63, p. 250–257.

Buddington, A. F., Jensen, M. L., and Mauger, R. L., 1969, Sulfur isotopes and origin of northwest Adirondacks sulfide deposits, *in* Igneous and Metamorphic Geology—a volume in honor of Arie Poldervaart: Geological Society of America Memoir 115, p. 423–451.

Carl, J. D., 1988, Popple Hill Gneiss as dacitic volcanics: A geochemical study of mesosome and leucosome, northwest Adirondacks, New York: Geological Society of America Bulletin, v. 100, p. 841–849.

Carl, J. D., and Van Diver, B. B., 1975, Precambrian Grenville alaskite bodies as ash-flow tuffs, northwest Adirondacks, New York: Geological Society of America Bulletin, v. 86, p. 1691–1707.

Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, p. 199–260.

Clayton, R. N., and Mayeda, T. K., 1963, The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis: Geochimica et Cosmochimica Acta, v. 22, p. 43–52.

Clayton, R. N., O'Neil, J. R., and Mayeda, T. K., 1972, Oxygen isotope exchange between quartz and water: Journal of Geophysical Research, v. 77, p. 3057–3067.

Degens, E. T., 1969, Biogeochemistry of stable carbon isotopes, *in* Eglinton, G., and Murphy, J. T. J., eds., Organic Geochemistry: Berlin-Heidelberg-New York, Springer, p. 304–329.

deLorraine, W. D., ms, 1979, Geology of the Fowler orebody, Balmat #4 mine, northwest Adirondacks, New York: Master's thesis, University of Massachusetts, Amherst, 159 p.

deLorraine, W. D., and Dill, D. B., Jr., 1982, Structure, stratigraphic controls and genesis of the Balmat zinc deposit, northwest Adirondacks, New York, *in* Hutchinson, R. W., and others, eds., Precambrian Sulphide Deposits, H. S. Robinson Memorial Volume: Geological Association of Canada Special Paper 25, p. 571–596.

Doe, B. R., 1962, Distribution and composition of sulfide minerals at Balmat, New York: Geological Society of America Bulletin, v. 73, p. 833–854.

Engel, A. E. J., and Engel, C. G., 1953a, Grenville series in the northwest Adirondack Mountains, New York: Part I, General features of the Grenville Series: Geological Society of America Bulletin, v. 64, p. 1013–1047.

———— 1953b, Grenville series in the northwest Adirondack Mountains, New York: Part II, Origin and metamorphism of the major paragneiss: Geological Society of America Bulletin, v. 64, p. 1049–1097.

Fletcher, I. R., and Farquhar, R. M., 1977, Lead isotopes in the Grenville and adjacent Paleozoic formations: Canadian Journal of Earth Science, v. 14, p. 56–66.

Foose, M. P., ms, 1974, The structure, stratigraphy, and metamorphic history of the Bigelow area, northwest Adirondacks, New York: Ph.D. thesis, Princeton University, 224 p.

Fritz, P., Drimmie, R. J., and Nowicki, V. K., 1974, Preparation of sulfur dioxide for mass spectrometric analysis by combustion of sulfides with copper oxide: Analytical Chemistry, v. 46, p. 164–166.

Goldhaber, M. B., and Kaplan, I. R., 1974, The sulfur cycle, *in* Goldberg, E. D., ed., The Sea, v. 5: New York, John Wiley & Sons, Inc., p. 569–655.

———— 1975, Controls and consequences of sulfate reduction in recent marine sediments: Soil Science, v. 119, p. 42–55.

———— 1980, Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California: Marine Chemistry, v. 9, p. 95–143.

Goodfellow, W. D., and Jonasson, I. R., 1984, Ocean stagnation and ventilation defined by $\delta^{34}S$ secular trends in pyrite and barite, Selwyn Basin, Yukon: Geology, v. 12, p. 583–586.

Grant, N. K., Lepak, R. J. Maher, T. M., Hudson, M. R., and Carl, J. D., 1986, Geochronological framework for the Grenville rocks of the Adirondack Mountains: Geological Society of America Annual Meeting, Abstracts with Programs, v. 18, p. 620.

Handford, C. R., 1981, A process-sedimentary framework for characterizing recent and ancient sabkhas: Sedimentary Geology, v. 30, p. 255–265.

Hoff, J. A., ms, 1984, Strontium isotope and trace element variations through the Upper Marble, Balmat, New York: M.S. thesis, Miami University, 133 p.

Hoff, J. A., Grant, N. K., and Whelan, J. F., 1984, Strontium and sulfur isotope variations in the Grenville marbles of the Balmat-Edwards district, northwestern New York: Geological Society of America Annual Meeting, Abstracts with Programs, v. 16, p. 541.

Holland, H. D., 1979, The solubility and occurrence of non-ore minerals, *in* Barnes, H. L., ed, Geochemistry of Hydrothermal Ore Deposits, 2d ed.: New York, John Wiley & Sons, p. 461–508.

———— 1978, The chemistry of the atmosphere and oceans: New York, John Wiley & Sons, Inc., 351 p.

Holser, W. T., 1977, Catastrophic chemical events in the history of the ocean: Nature, v. 267, p. 403–408.

———— 1979, Mineralogy of evaporites, *in* Burns, R. G., ed, Marine Minerals: Mineralogical Society of America, Reviews in Mineralogy, v. 6, p. 211–294.

Holser, W. T., and Kaplan, I. R., 1966, Isotope geochemistry of sedimentary sulfates: Chemical Geology, v. 1, p. 93–105.

Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I., 1979, Isotope geochemistry of oxygen in the sedimentary sulfate cycle: Chemical Geology, v. 25, p. 1–17.

Holser, W. T., Schidlowski, M., Mackenzie, F. T., and Maynard, J. B., 1988, Biogeochemical cycles of carbon and sulfur, *in* Gregor, C. B., and others, eds., Chemical Cycles in the Evolution of the Earth: New York, John Wiley & Sons, Inc., p. 105–174.

Holt, B. D., and Engelkemeir, A. G., 1970, Thermal decomposition of barium sulfate to sulfur dioxide for mass spectrometer analysis: Analytical Chemistry, v. 42, p. 1451–1453.

Houghton, M. L., ms, 1980, Geochemistry of the Proterozoic Hormuz evaporites, southern Iran: Master's thesis, University of Oregon, 85 p.

Hovorka, S., 1987, Depositional environments of marine-dominated bedded halite, Permian San Andres formation, Texas: Sedimentology, v. 34, p. 1029–1054.

Hudson, J. D., 1977, Stable isotopes and limestone lithification: Journal of the Geological Society of London, v. 133, p. 636–660.

Isachsen, Y. W., and Landing, E., 1983, First Proterozoic stromatolites from the Adirondack Massif: Stratigraphic, structural, and depositional implications: Geological Society of America Northeastern Meeting, Abstracts with Programs, v. 13, p. 210.

Kaplan, I. R., Emery, K. O., and Rittenberg, S. C., 1963, The distribution and isotopic abundance of sulfur in recent marine sediments off southern California: Geochimica et Cosmochimica Acta, v. 27, p. 297–331.

Kelts, K., 1988, Environments of deposition of lacustrine petroleum source rocks, an introduction, *in* Fleet, A. J., and others, eds, Lacustrine Petroleum Source Rocks: Geological Society Special Publication 40, p. 3–26.

Kendall, A. C., 1984, Evaporites, *in* Walker, R. G., ed., Facies Models: Geoscience Canada Reprint Series 1, p. 259–296.

Kieth, M. L., and Weber, J. N., 1964, Carbon and oxygen isotopic composition of selected limestones and fossils: Geochimica et Cosmochimica Acta, v. 28, p. 1787–1816.

Kinsman, D. J. J., 1975, Salt floors to geosynclines: Nature, v. 255, p. 375–378.

Knauth, L. P., and Lowe, D. R., 1978, Oxygen isotope geochemistry of cherts from the Onverwacht group (3.4 billion years), Transvaal, South Africa, with implications for secular variations in the isotopic composition of cherts: Earth and Planetary Science Letters, v. 41, p. 209–222.

Krogh, T. E., and Hurley, P. M., 1968, Strontium isotope variation and whole-rock isochron studies, Grenville Province of Ontario: Journal of Geophysical Research, v. 73, p. 7107–7125.

Lea, E. R., and Dill, D. B., Jr., 1968, Zinc deposits of the Balmat-Edwards districts, N.Y., *in* Ridge, J. D., ed., Ore Deposits of the United States, 1933–1967 (Graton-Sales volume): New York, American Institute of Mining, Metallurgy, and Petroleum Engineers, v. 1, p. 20–48.

Lloyd, R. M., 1968, Oxygen isotope behavior in the sulfate-water system: Journal of Geophysical Research, v. 18, p. 6099–6110.

Makela, M., 1974, A study of sulfur isotopes in the Outokumpo ore deposit, Finland: Geological Survey of Finland Bulletin 267, 45 p.

Mezger, K., Bohlen, S. R., and Hansen, G. N., 1988, U-Pb garnet, monazite, and rutile ages: implications for the duration of high-grade metamorphism and cooling histories, Adirondack Mts. New York: Geological Society of America Annual Meeting, Abstracts with Programs, v. 20, p. A-100.

McCrea, J. M., 1950, The isotopic chemistry of carbonates and a paleotemperature scale: Journal of Chemical Physics, v. 18, p. 849–857.

Nehring, N. L., Bowen, P. A., and Truesdell, A. H., 1977, Techniques for the conversion to carbon dioxide of oxygen from dissolved sulfate in thermal waters: Geothermics, v. 5, p. 63–66.

Nielsen, H., 1978, Sulfur-isotopes in nature, *in* Wedepohl, K. H., ed., The Handbook of Geochemistry, v. II: Berlin, Springer-Verlag, chapter 16-B, 40 p.

Northrop, D. A., and Clayton, R. N., 1966, Oxygen-isotope fractionations in systems containing dolomite: Journal of Geology, v. 74, p. 174–196.

Orr, W. L., 1977, Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas, *in* Campos, R., and Goni, J., eds., Advances in Organic Geochemistry—1975; Proceedings of a Conference held in Madrid, Spain, p. 571–597.

Palmer, M. R., and Slack, J. F., in press, Boron isotopic composition of tourmaline from massive sulfide deposits and tourmalinites: Contributions to Mineralogy and Petrology.

Prucha, J. J., 1957, Pyrite deposits of St. Lawrence and Jefferson Counties, N. Y.: New York State Museum Bulletin 357 p.

Romey, R., and Jacoby, R. S., 1978, Large-scale "Grenville" nappe structures involving gneisses in southeastern Ontario and the northwest Adirondack Lowlands: Geological Society of America Annual Meeting, Abstracts with Programs, v. 10, p. 480.

Sasaki, A., 1972, Variation in sulfur isotopic composition of oceanic sulfate: International Geological Congress, 24th, Montreal, 1972, section 10, p. 342–345.

Schmalz, R. F., 1969, Deep-water evaporite deposition: A genetic model: American Association of Petroleum Geologists Bulletin, v. 53, p. 798–823.

Schreiber, B. C., 1978, Environments of subaqueous gypsum deposition, *in* Dean, W. E., and Schreiber, B. C., eds., Marine Evaporites: Society of Economic Paleontologists and Mineralogists Short Course No. 4, Oklahoma City, p. 43–73.

Shanks, W. C., and Bischoff, J. L., 1980, Geochemistry, sulfur isotope composition, and accumulation rates of Red Sea geothermal deposits: Economic Geology, v. 75, p. 45–459.

Shanks, W. C., Woodruff, L. G., Jilson, G. A., Jennings, D. S., Modene, J. S., and Ryan, B. D., 1987, Sulfur and lead isotope studies of stratiform Zn-Pb-Ag deposits, Anvil Range, Yukon: Basinal brine exhalation and anoxic bottom-water mixing: Economic Geology, v. 82, p. 600–634.

Smith, J. W., and Croxford, N. J. W., 1973, Sulphur isotope ratios in the McArthur lead-zinc-silver deposit: Nature, v. 245, p. 10–12.

Swihart, G. H., and Moore, P. B., 1989, A reconnaissance of the boron isotopic composition of tourmaline: Geochimica et Cosmochimica Acta, v. 53, p. 911–916.

Thode, H. G., Monster, J., and Dunford, H. B., 1961, Sulfur isotope geochemistry: Geochimica et Cosmochimica Acta, v. 25, p. 159–174.

Thode, H. G., and Monster, J., 1965, Sulfur isotope geochemistry of petroleum, evaporites, and ancient seas: American Association of Petroleum Geologists Memoir 4, p. 307–317.

Valley, J. W., and O'Neil, J. R., 1984, Fluid heterogeneity during granulite facies metamorphism in the Adirondacks: stable isotope evidence: Contributions to Mineralogy and Petrology, v. 85, p. 158–173.

Veizer, J., and Compston, W., 1976, $^{87}Sr/^{86}Sr$ in Precambrian carbonates as an index of crustal evolution: Geochimica et Cosmochimica Acta, v. 40, p. 905–914.

Von Damm, K. L., Edmond, J. M., Measures, C. I., and Grant, B., 1985, Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California: Geochimica et Cosmochimica Acta, v. 49, p. 2221–2237.

Walker, R. N., Muir, M. D., Diver, W., and Williams, N., 1977, Evidence of major sulphate evaporite deposits in the Proterozoic McArthur River Group, Western Territory, Australia: Nature, v. 265, p. 526–529.

Whelan, J. F., Rye, R. O., and deLorraine, W., 1984, The Balmat-Edwards zinc-lead deposits—synsedimentary ore from Mississippi Valley-type fluids: Economic Geology, v. 79, p. 239–265.

Williams, N. and Rye, D. M., 1974, Alternative interpretation of sulphur isotope ratios in the McArthur lead-zinc-silver deposit: Nature, v. 247, p. 535–537.

Wiener, R. W., McLelland, J. M., Isachsen, Y. W., and Hall, L. M., 1984, Stratigraphy and structural geology of the Adirondack Mountains, New York: Review and analysis: Geological Society of America Special Paper 194, p. 1–55.

Zak, I., Sakai, H., and Kaplan, I. R., 1980, Factors controlling the $^{18}O/^{16}O$ and $^{34}S/^{32}S$ isotope ratios of ocean sulfates, evaporites and interstitial sulfates from modern deep-sea sediments: Isotope Marine Chemistry, p. 339–373.