

Geochemistry of a 1.2 Ga carbonate-evaporite succession, northern Baffin and Bylot Islands: implications for Mesoproterozoic marine evolution

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Abstract

A 4‰ positive shift in the carbon isotopic composition of the oceans, recorded globally in marine carbonate rocks at ~1.3 Ga, suggests a significant change in Mesoproterozoic carbon cycling. Enhanced burial fluxes of organic carbon, relative to inorganic carbon, implied by this isotopic shift may have resulted in increased oxygenation of the Earth's biosphere, as has been suggested for similar Paleoproterozoic and Neoproterozoic carbon isotope events. This hypothesized Mesoproterozoic oxygenation event may be recorded in the geologic record by the appearance of the oldest preserved, laterally extensive, bedded marine CaSO₄ evaporites in the ~1.2 Ga Grenville and Bylot supergroups. Speculation that the appearance of extensively preserved marine gypsum and/or anhydrite reflects increased biospheric oxygenation has been challenged, however, by the hypothesis that CaSO₄ precipitation prior to the Mesoproterozoic may have been inhibited by significantly higher marine carbonate saturation, which would have facilitated carbonate precipitation and effectively limited Ca²⁺ availability during seawater evaporation (Grotzinger, J.P., 1989. Controls on Carbonate Platform and Basin Development, vol. 44, SEPM, Tulsa, OK, pp. 79–106), regardless of O₂ levels. The 1.2 Ga Society Cliffs Formation (Bylot Supergroup, northern Baffin Island) consists of ~720 m of peritidal carbonates, evaporites, and minor siliciclastic rocks. Evaporites occur predominantly in the lowermost 300 m of the Society Cliffs Formation, where gypsum beds (1–250 cm thick) constitute up to 15% of the exposed strata. Stratigraphic and sedimentologic constraints, as well as isotopic (C, O, Sr) and elemental (Ca, Sr, Na, K, Ba) compositions of evaporites and associated carbonates, indicate a marine origin for Society Cliffs gypsum. An upsection increase in δ³⁴S of Society Cliffs gypsum (from +22‰ to +32‰ VCDT) is therefore interpreted to reflect primary variation in Mesoproterozoic marine sulfate compositions, although the inferred rapidity of isotopic change requires a marine sulfate reservoir significantly smaller than that of the modern ocean. Examination of the maximum fractionation between coeval sulfide and sulfate reservoirs, however, indicates that Mesoproterozoic oceans were not sulfate-limited with respect to bacterial sulfate reduction either before or after the hypothesized 1.3 Ga oxygenation event. Although increased ocean-atmosphere oxygenation may have increased marine sulfate concentrations at this

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time, the exact role of a Mesoproterozoic oxygenation event cannot be ascertained. Furthermore, high Mg/Ca ratios measured in Society Cliffs gypsum suggest that elevated Mg^{2+} concentrations in Proterozoic marine systems may have helped sustain carbonate hypersaturation, and that Ca^{2+} -limitation may have played a significant role in the Proterozoic record of evaporite deposition. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Isotopic and elemental compositions have long been used to infer the depositional and diagenetic histories of marine carbonate and evaporite minerals (Land, 1980; Veizer, 1983; Grotzinger and Read, 1983; Fairchild and Spiro, 1987; Banner et al., 1988; Banner, 1995; Frank and Lohmann, 1996). Even as primary variation in the mineralogy and isotopic composition of carbonate and evaporite minerals is postulated to reflect changes in seawater composition through time (Veizer et al., 1980; Wilkinson and Given, 1986; Veizer, 1989; Kaufman and Knoll, 1995; Hardie, 1996; Veizer et al., 1997), Phanerozoic marine waters likely remained within relatively limited compositional bounds (Holland, 1972; Spencer and Hardie, 1990). Fundamental uncertainties remain, however, as to the constancy of marine compositions earlier in Earth history. Resolution of these fundamental uncertainties is critical to interpreting the driving mechanisms of biospheric evolution, including changing carbonate chemistry, nutrient cycling, and biotic evolution.

The difficulty of determining seawater chemistry in pre-Phanerozoic carbonate systems is typically exacerbated by the absence of shelly fossils, the presence of unconventional depositional fabrics (e.g., seafloor precipitates: Grotzinger, 1993; Bartley et al., 2000; herringbone carbonate: Sumner and Grotzinger, 1996a,b; molar-tooth carbonate: Furniss et al., 1997), and the often ubiquitous early dolomitization of carbonate components. Interpretation of evaporitic successions is further complicated by the restricted nature of their deposition and the complexity of brine interactions upon evaporation, which obscures the composition of parent fluids (Hardie and Eugster, 1970; Holland et

al., 1997), as well as by their high solubility, which typically results in non-preservation of the late-stage evaporite phases required to accurately reconstruct brine compositions (Hardie, 1984).

The ~1.2 Ga Society Cliffs Formation, northern Baffin and Bylot Islands, Canada, consists of a thick (> 720 m) succession of carbonate rocks, which contain some of the oldest preserved bedded $CaSO_4$ evaporites and thus provides a unique opportunity to investigate the geochemical composition of the Mesoproterozoic ocean. Previous stratigraphic (Kah, in press) and geochemical investigation (Kah et al., 1999; Kah, 2000) of Society Cliffs carbonate rocks has helped constrain environments of deposition and diagenesis, and has demonstrated our ability to infer primary geochemical compositions from dominantly dolomitic lithologies. In the current study, we present new C isotope data from peritidal carbonate rocks on Bylot Island, which assists in the correlation of this succession with previously examined rocks on Baffin Island. We then combine stratigraphic, sedimentologic, isotopic, and elemental data to constrain the origin of brines from which Society Cliffs evaporite minerals precipitated in order to infer primary geochemical characteristics of Mesoproterozoic seawater. Finally, these data are used to test hypotheses regarding ocean-atmosphere oxidation, changing marine carbonate saturation, and the evolution of the Proterozoic evaporite record.

2. Geologic setting

2.1. Regional geology

The Society Cliffs Formation is the lowermost carbonate unit in the Bylot Supergroup, a thick

package (> 6000 m) of unmetamorphosed and nearly undeformed siliciclastic and carbonate rocks exposed within the fault-bounded Borden Basins of northern Baffin and Bylot Islands (Fig. 1). Sedimentary rocks of the predominantly siliciclastic Eqaalulik Group, the carbonate dominated Uluksan Group, and the siliciclastic Nunatsiaq Group record a complex history of rifting (Jackson et al., 1980; Jackson and Iannelli, 1981), localized tectonic uplift (Jackson et al., 1978; Iannelli, 1979), sea level fluctuations (Narbonne and James, 1996), and periods of regional stability (Geldsetzer, 1973; Knight and Jackson, 1994). Biostratigraphic (Hofmann and Jackson, 1994), chemostratigraphic (Kah et al., 1999), paleomagnetic (Fahrig et al., 1971, 1981; Christie and Fahrig, 1983; Pehrsson and Buchan, 1993), and radiometric (Jackson, 1974; LeCheminant and Heaman, 1989; Heaman et al., 1992) studies indicate deposition of the Bylot Supergroup between ~1270 and 1000 Ma. Recent Pb–Pb dating of sedimentary carbonates yielded ages of 1199 ± 24 Ma for deposition of the Society Cliffs Formation and 1204 ± 22 for combined Society Cliffs and

overlying Victor Bay and Athole Point formations (Kah and Marcantonio, unpublished data).

2.2. Stratigraphy and depositional setting

2.2.1. Society Cliffs strata on Baffin Island

The Society Cliffs Formation comprises the most laterally extensive package of carbonate rocks in the Bylot Supergroup and records shallow subtidal to supratidal deposition of carbonates, fine-grained siliciclastics, evaporites, and microfossil-bearing early diagenetic chert (Hofmann and Jackson, 1991; Kah and Knoll, 1996). The formation conformably to unconformably overlies marine shale and carbonate of the Arctic Bay Formation, and is overlain abruptly, on Baffin Island, by up to 100 m of pyritic black shale and subtidal carbonate lithologies of the basal Victor Bay Formation (Jackson and Iannelli, 1981).

On Baffin Island, Society Cliffs strata represent deposition in mid-ramp and inner-ramp environments within three stratigraphically discrete carbonate packages (Kah, in press). The lower

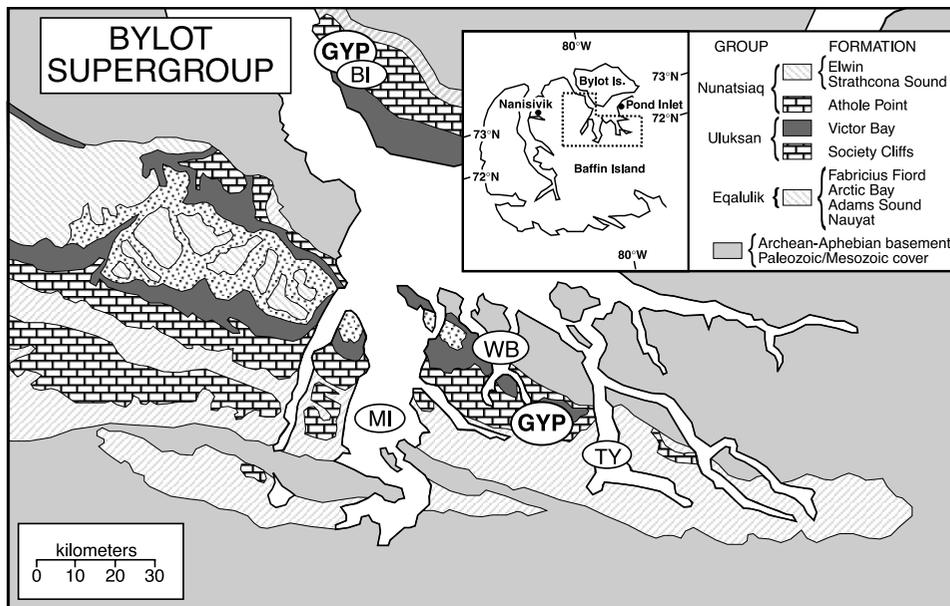


Fig. 1. Geologic map of the Bylot Supergroup, northern Baffin and Bylot Islands. Isotopic and elemental analyses in this paper are from carbonate and evaporite minerals (GYP) collected from measured sections on Bylot Island (BI) and between White Bay (WB) and Tay Sound (TS). Milne Inlet (MI) is labeled for reference.

Society Cliffs platform (~200 m thick) consists of four aggradational, unconformity-bounded sequences representing initial flooding of the Society Cliffs platform. Inner ramp facies record cyclic deposition of shallow subtidal to intertidal stromatolitic dolostone; intertidal to supratidal deposition of microbially laminated dolostone containing evaporite nodules and thin, cataclastic deposits interpreted as evaporite collapse breccias; and supratidal deposition of mudcracked, red shale. Occasionally, laminated gypsum (up to 150 cm thick) occurs at the interface between microbial dolostone and overlying terrigenous sediments and, rarely, within shale intervals. Mid-ramp facies consist largely of black shale and microbreccia carbonate grainstone, interpreted as lowstand deposition of terrigenous material and incised platform margin carbonates (Kah, in press).

A single depositional sequence (~125 m thick) marks the transition to the Society Cliffs upper platform. Initiation of ooid development in mid-ramp facies and a marked landward shift of terrigenous facies indicate increased water depth across the platform. In this sequence, evidence for evaporite development is largely absent, and deposition is dominated by thinly laminated microbial carbonate and microlaminated seafloor cements (Kah, in press). Progradation of a thick (~50 m) red shale package and deposition of lowstand black shale/microbreccia facies mark the end of this transitional sequence.

Development of the Society Cliffs upper platform is marked by additional flooding of the platform followed by deposition of eight unconformity-bounded sequences (Kah, in press). Absence of terrigenous input to much of the upper platform, with the exception of a thin red shale at 600 m and rare quartz stringers between 600 and 720 m, indicates a continued landward shift of terrigenous facies. Increased water depths are indicated by a shift in the primary locus of carbonate deposition from inner ramp facies to mid-ramp facies. Mid-ramp facies consist of 1–10 m aggradational cycles of columnar stromatolites, oolitic and intraclastic grainstones, and thinly bedded micrite, capped by tepees and desiccation polygons. In contrast, inner ramp facies are dom-

inated by 10–50 m cycles consisting of a mosaic of stromatolitic dolostone, thinly laminated microbial carbonate, and microlaminated seafloor cements. Inner ramp carbonates were likely deposited in situ within an evaporative microbial flat that was frequently restricted from open marine waters by subaerial exposure of the mid-ramp shoal complex (Kah, in press).

2.2.2. *Society Cliffs strata on Bylot Island*

Carbonate strata exposed on northern and western Bylot Island are described in previous studies as undifferentiated Society Cliffs-Victor Bay (Jackson and Cumming, 1981; Jackson and Iannelli, 1981). These strata consist of ~740 m of mixed carbonate, siliciclastic, and evaporite strata (Fig. 2) overlain by ~75 m of red shale, and >1500 m of dominantly siliciclastic lithologies. The basal 200 m of carbonate strata consist of 10–50 m cycles of stromatolitic carbonate, shaly carbonate, abundant bedded gypsum, carbonate seafloor cements, and rare chert. Overlying this basal succession is a thick non-cyclic interval (~150–200 m) composed of 50 m of stromatolitic and microbially laminated dolostone overlain by 50 m of black shale containing rare carbonate and gypsum interbeds, which grade upward into a covered interval containing rare outcrops of red and green shale with abundant halite casts. A major flooding surface at ~400 m marks the appearance of significantly different carbonate facies and the onset of a greater frequency of cyclicity (1–20 m cycles). Facies include massively bedded micrite, seafloor precipitates, a single interval of 'molar-tooth' carbonate (Furniss et al., 1997; James et al., 1998), microbially laminated carbonate with rare cauliflower chert and jasper, cross-bedded oolitic grainstone with up to 5% quartz sand and jasper grains, and mudcracked red shale with rare halite casts.

2.2.3. *Correlation of Society Cliffs strata*

Correlation between Society Cliffs strata on Baffin Island and Bylot Island is suggested by three lines of evidence: (1) similarity of facies patterns and occurrences of specific lithological marker beds (asterisks, Fig. 2), (2) similarity of scales of cyclicity, small-scale cycle packaging,

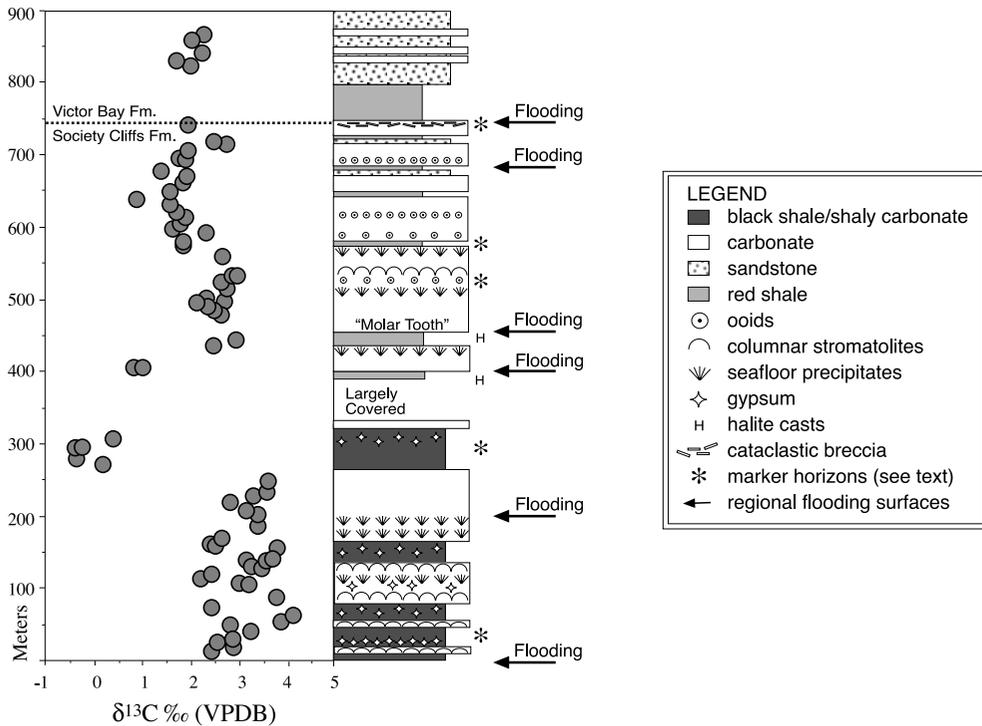


Fig. 2. Bylot Island chemostratigraphy and generalized stratigraphy. Moderately positive $\delta^{13}\text{C}$ values lack the 3–4‰ variation that marks deposition of Victor Bay and Athole Point formations, and are consistent with deposition coeval with Society Cliffs strata on Baffin Island (cf. Fig. 4 of Kah et al., 1999). Arrows indicate position of regionally traceable flooding surfaces, and asterisks mark distinct lithologic occurrences used in correlation of the Society Cliffs Formation section on Bylot Island with Society Cliffs sections on Baffin Island (e.g., Milne Inlet and Tay Cliffs sections, labeled on Fig. 1).

and location of flooding surfaces (arrows, Fig. 2), and (3) carbon isotope chemostratigraphy (Fig. 2). Lithologic markers include a single thick (150–200 cm) gypsum bed at ~25 m, a thick (>25 m) terrigenous interval at ~300 m, increasingly abundant oolitic facies in upper half of the succession, recurrence of siliciclastic influx at ~580 m, and a single 1.5 m thick cataclastic breccia located at ~725 m. Regionally traceable stratigraphic surfaces include the basal contact with underlying Arctic Bay black shale; major flooding surfaces at ~200, 400, 450, and 680 m; and an upper contact with a >50 m thick shale interval of the basal Victor Bay Formation (Kah, in press). Finally, carbonate strata from Bylot Island record moderately positive $\delta^{13}\text{C}$ values ($3.0 \pm 1.0\text{‰}$) which show a broad monotonic decline from basal values near +4‰ to values < +3‰ at the top of the section (cf.

Kah et al., 1999). Although C isotope values show greater variability and minor depletion with respect to those recorded in Society Cliffs mid-ramp carbonates from Milne Inlet, values are consistent with those recorded in inner-ramp carbonates from White Bay and Tay Cliffs (Kah et al., 1999; Kah, unpublished data). Kah et al. (1999) interpreted minor ^{13}C depletion in inner ramp carbonates as reflecting an increased ^{12}C contribution from degrading microbial mats during local carbonate precipitation. Overall, moderately positive C isotope values are consistent with profiles from Society Cliffs carbonates, and are inconsistent with C isotope trends recorded in overlying Victor Bay and Athole Point formations, which contain no isotopic values > +2.7‰ and which record several abrupt negative excursions followed by prolonged intervals of recovery (Kah et al., 1999).

2.3. Evaporite facies

Evaporite facies in the Society Cliffs Formation occur predominantly in the lowermost 300 m of Society Cliffs strata on Bylot Island, where gypsum beds (1–250 cm thick) constitute up to 15% of the preserved strata. Gypsum occurs as laterally continuous, massive (Fig. 3(A)) to laminated beds (Fig. 3(B)) near the tops of shoaling cycles. Gypsum beds are underlain by microbially lami-

nated to stromatolitic marine carbonates and are commonly interbedded with carbonate precipitate structures (Fig. 3(C); Kah, in press). Gypsum occurrences are typically overlain by strata containing evidence for subaerial exposure, such as mudcracked shale horizons with abundant halite casts (Fig. 3(D)) and tepee-cracked or brecciated carbonate pavements.

Most evaporite occurrences contain thin laminae (0.5–5 cm) alternating with organic laminae

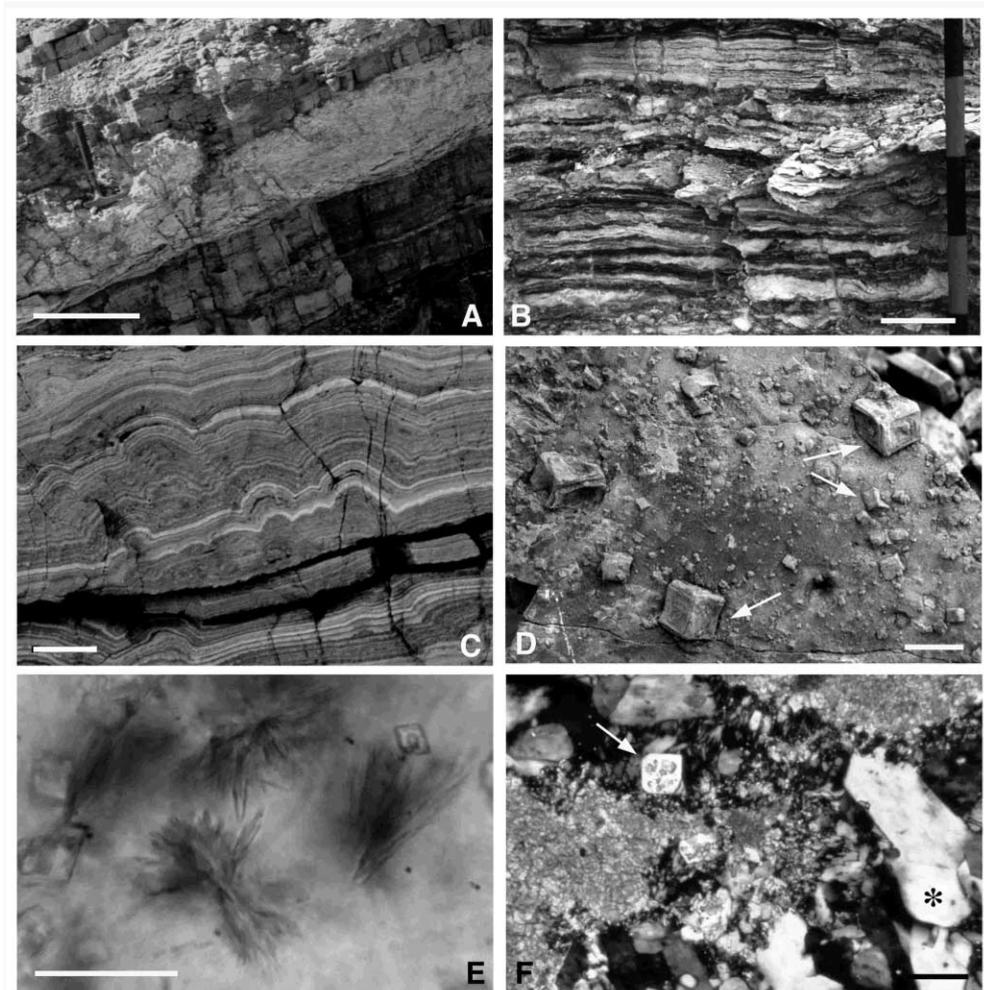


Fig. 3. Evaporitic lithologies from the Society Cliffs Formation, Bylot Island: (A) thickly bedded, massive gypsum (scale bar = 35 cm); (B) thinly bedded gypsum interbedded with organic-rich carbonate (scale bar = 10 cm); (C) sea-floor carbonate precipitates, a common lithological association (scale bar = 1.5 cm); (D) halite hoppers (arrows) in red shale overlying gypsiferous lithologies (scale bar = 1.5 cm); (E) pseudomorphic gypsum lathe rosettes preserved in early diagenetic chert (scale bar = 50 μ m); (F) silicified halite cube (arrow) retained within a small gypsum nodule (asterisk; scale bar = 150 μ m).

and shaly carbonate. Laminae are typically planar to slightly crenulated, show no evidence of clastic transport textures, and only rarely contain small enterolithic folds, tepee structures, and microkarstic surfaces. Although laminated gypsum can precipitate either in the water column or within upper layers of the substrate, pseudomorphs of bottom-nucleated lathes (2–5 cm high) and delicate gypsum rosettes (Fig. 3(E)) replaced by early diagenetic chert suggest formation within the water column. Occasionally, however, laminated to massive gypsum displays a pseudo-nodular morphology and incorporates various amounts carbonate or siliclastic sediment, suggesting precipitation within the sediment matrix. Interstitial, displacive growth is also indicated by the occurrence of small (1–4 cm) dolomitized vugs within microbially laminated carbonate and micritic laminae that contain dolomitic lenticular pseudomorphs after gypsum (cf. Fig. 5(e) and (f) of Kah, 2000). Rarely, gypsum nodules preserve silicified halite cubes (Fig. 3(F)). Together, the relationship of gypsum to overlying supratidal and underlying subtidal to intertidal facies, the occurrence of both bottom-nucleated and displacive textures, and rare evidence for subaerial exposure suggest deposition in subaqueous marginal-marine to sabkha environments.

3. Geochemical procedures

3.1. C and O isotope analyses

Analytical methods for preparation of Society Cliffs Formation carbonate samples are detailed elsewhere (Kah et al., 1999; Kah, 2000) and summarized below. Paired thin and polished thick sections were prepared for all samples. Thin sections were evaluated petrographically in order to characterize preservation of individual carbonate phases. These phases were then evaluated via standard cathodoluminescence to assess degree of alteration and recrystallization. With rare exception, carbonate samples lack zoned cements or late-stage spar and display uniformly dull luminescence across the various carbonate

phases. Microsampled powders were then prepared by drilling dull luminescent phases with 500 μm and 1 mm diamond drill bits. C and O isotope determinations were performed on <0.5 mg aliquots of microdrilled powder at Mountain Mass Spectrometry, Inc., using a VG Optima gas source mass spectrometer fitted with a Multiprep device for on-line acidification of sample powders. Isotopic compositions are presented in standard delta notation as permil (‰) deviations from VPDB, with analytical error < 0.1‰, calculated from replicate analyses of a laboratory standard.

3.2. S isotope analyses

Isotopic and elemental analyses of gypsum were performed on whole-rock samples. Initially, all samples were broken into sub-mm pieces, examined under low power magnification, and picked free of visible non-evaporite phases. Samples were then crushed to <35 μm powder in a Spex milling machine and rinsed with ethanol to remove fluids liberated from inclusions during crushing (Lu et al., 1997). Approximately 20 mg of powder were dissolved in ultrapure water and reprecipitated as BaSO_4 by addition of a saturated BaCl solution. Rinsed, filtered, and dried BaSO_4 precipitates were combined with an excess of V_2O_5 and analyzed for S-isotopic composition at Indiana University on a Finnigan MAT 252 gas source mass spectrometer fitted with a peripheral elemental analyzer (EA) for on-line sample combustion.

Powdered whole-rock black shale and shaly carbonate samples were also analyzed. C_{org} concentrations were measured via standard coulometric methods. Concentrations of disseminated pyrite within were quantified via standard chromium-reduction methods (Canfield et al., 1986). Additional aliquots were reduced by these same methods but with the liberated sulfide precipitated as Ag_2S (Newton et al., 1995). Ag_2S was homogenized with cupric oxide and combusted under vacuum for quantitative conversion to sulfur dioxide. S isotopic compositions for pyrite were determined at the University of

Missouri using a Finnigan MAT Delta E gas source mass spectrometer. All S isotopic compositions are expressed in standard delta-notation as permil (‰) deviations from VCDT, with analytical error of $< 0.01\text{‰}$ for sulfate and $< 0.1\text{‰}$ for sulfide samples, calculated from replicate analyses of laboratory standards.

3.3. Sr isotope analyses

Sr isotopic analyses were performed on all gypsum samples. 10–15 mg rinsed and filtered gypsum powder were dissolved in ultrapure water, resulting in Sr concentrations in solution of roughly 1–1.5 $\mu\text{g/ml}$. Although empirical evidence suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios can easily be contaminated by the presence of terrigenous material (Derry et al., 1992; Montañez et al., 1996), high concentrations of Sr in gypsum (typically > 1000 ppm) and sample dissolution in ultrapure water are believed to have minimized contamination from minute quantities of terrigenous material. Additionally, a survey of six samples with low Sr indicated that ^{87}Rb levels were too low to have contributed significantly to ^{87}Sr measurements. Solution aliquots of ~ 1 ml were extracted, and Sr was isolated via standard cation exchange methods. 500–1000 ng of purified Sr were loaded onto Ta filaments, and $^{87}\text{Sr}/^{86}\text{Sr}$ compositions were determined via thermal ionization using a VG Sector 54 multicollector mass spectrometer at the University of Arizona. Multiple analyses of Sr standard NBS-987 during the course of sample analysis averaged 0.710256 ± 0.000009 .

3.4. Elemental analyses

Analyses of major and trace elements were performed on all carbonate and gypsum samples. Aliquots of microdrilled carbonate (typically 0.5–2.0 mg) were dissolved in 2.5 ml ultrapure 2 N HNO_3 . Solutions were then centrifuged, and 2.0 ml were decanted to avoid insoluble residue. For gypsum, ~ 12 mg of powder were dissolved in 15 ml ultrapure water and agitated at room temperature for several hours. Solutions were then centrifuged, and 5 ml were decanted to

avoid solid residues. Concentrations of major and trace elements (Ca, Mg, Sr, Mn, Fe; plus Ba, Na, and K in gypsum) were measured at the University of Missouri using a Perkin–Elmer inductively-coupled plasma-atomic emission spectrometer (ICP-AES) fitted with a micro-concentric nebulizer and calibrated to a series of gravimetrically determined standards. Reproducibility, determined via replicate analyses of sample and standard solutions, was better than 5% for Sr, Mn, and Ba, and better than 10% for Ca, Mg, Fe, Na, and K.

4. Analysis of geochemical results

4.1. Depositional and diagenetic trends of Society Cliffs carbonates

Unlike the carbon isotopic composition of ancient marine carbonate rocks, which is commonly buffered near marine values by the typically low carbon content of most diagenetic fluids (Kaufman et al., 1991; Frank and Lohmann, 1996), variation in trace element concentration and oxygen isotopic composition often results from interaction with non-marine fluids. Furthermore, isotopic and elemental variation typically follows diagnostic trends that reflect (1) the relative abundance of elements in the parent carbonate and reacting fluids, and (2) the extent of water-rock interaction (Brand and Veizer, 1980; Banner and Hanson, 1990). Documenting the extent of geochemical and isotopic variability between petrographic components and within sample suites can therefore provide important constraints on the depositional and diagenetic history of carbonate samples and therefore on the primary compositions of marine source waters (Given and Lohmann, 1985; Zempolich et al., 1988; Carpenter et al., 1991; Frank and Lohmann, 1996; Kah, 2000).

Isotopic and elemental data for Society Cliffs carbonates from Bylot Island are summarized in Table 1. Overall, compositions of Bylot Island carbonates are strikingly similar to those of previously analyzed Society Cliffs samples (Figs. 2

Table 1
Carbonate isotopic and elemental compositions, Bylot Island

Sample ^a	Height (m)	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	Mg/Ca	Sr (ppm)	Mn (ppm)	Fe (ppm)
BY97-96	9.6	2.4	-1.5	0.59	123	378	1999
BY97-154	15.4	2.9	-0.1	0.57	114	303	2252
BY97-195	19.5	2.5	-0.8	0.58	94	339	3493
BY97-270	27.0	2.9	-1.6	0.49	356	289	1850
BY97-365	36.5	3.2	-0.9	0.57	183	297	3331
BY97-441	44.1	2.8	-1.4	0.37	347	282	1037
BY97-518	51.8	3.9	-1.5	0.55	104	253	1105
BY97-598	59.8	4.1	-1.1	0.58	100	337	2184
BY97-689	68.9	2.4	-0.6	0.62	110	110	576
BY97-838	83.8	3.8	-1.8	0.57	95	138	1292
BY97-1021	102.1	3.1	-1.6	0.55	124	146	745
BY97-1024	102.4	3.0	-1.0	0.71	117	107	586
BY97-1103	110.3	2.2	-1.2	0.59	86	499	882
BY97-1160	116.0	2.4	-1.8	0.57	121	295	870
BY97-1255	125.5	3.3	-1.9	0.57	111	164	855
BY97-1270	127.0	3.4	-2.5	0.56	71	211	1621
BY97-1313	131.3	3.5	-1.3	0.57	139	178	1279
BY97-1321	132.1	3.5	0.7	0.56	284	142	1115
BY97-1352A	135.2	3.1	-1.9	0.61	243	221	1672
BY97-1359	135.8	3.6	-0.6	0.59	150	105	681
BY97-1520	152.0	3.8	-1.7	0.55	107	133	713
BY97-1565A	156.5	2.3	-0.9	0.63	129	411	1474
BY97-1565B	156.5	2.5	-0.8	0.58	133	427	959
BY97-1650	165.0	2.6	-1.9	0.60	121	605	2415
BY97-1840	184.0	3.4	-1.1	0.57	112	141	1062
BY97-1986	198.6	3.3	-2.3	0.57	97	259	2408
BY97-2045	204.5	3.1	-2.6	0.57	111	250	2098
BY97-2150A	215.0	2.7	-3.2	0.55	121	375	2542
BY97-2150B	215.0	2.7	-3.1	0.60	157	276	806
BY97-2230	223.3	3.3	-5.0	0.55	36	334	2952
BY97-2320B	232.0	3.5	-3.2	0.55	85	281	2253
BY97-2428	242.8	3.6	-2.8	0.58	721	330	3419
BY97-2683	268.3	0.1	-2.8	0.59	77	239	6486
BY97-2774	277.4	-0.4	-2.7	0.60	45	316	7262
BY97-2902	290.2	-0.5	-3.3	0.60	58	268	7111
BY97-2916A	291.6	-0.3	-2.6	0.58	136	151	2611
BY97-2916B	291.6	-0.3	-2.6	0.62	123	191	4502
BY97-3044	304.4	0.4	-3.0	0.59	55	249	3486
BY97-4030A	403.0	0.8	-3.4	0.61	82	598	7698
BY97-4030B	403.0	1.0	-3.2	0.58	31	454	5793
BY97-4312	431.2	2.4	-2.8	0.55	74	321	4621
BY97-4406	440.6	2.9	-2.1	0.57	61	402	6910
BY97-4762A*	476.2	2.6	-4.6	0.04	1903	69	857
BY97-4762B	476.2	2.6	-4.4	0.40	282	307	5912
BY97-4762C*	476.2	2.6	-4.5	0.06	1392	100	2309
BY97-4807*	480.7	2.4	-3.7	0.03	1133	85	1349
BY97-4866	486.6	2.3	-1.0	0.61	111	174	3677
BY97-4925	492.5	2.1	-1.7	0.60	94	358	6913
BY97-4946	494.6	2.7	-1.7	0.56	87	161	3702
BY97-4989	498.9	2.3	-0.4	0.62	80	193	6556
BY97-5130	513.0	2.7	-2.3	0.56	55	120	1614
BY97-5210	521.0	2.6	-0.3	0.59	77	100	2368

Table 1 (Continued)

Sample ^a	Height (m)	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	Mg/Ca	Sr (ppm)	Mn (ppm)	Fe (ppm)
BY97-5305A	530.5	2.9	-0.4	0.56	90	58	620
BY97-5305B	530.5	2.9	-0.5	0.56	98	68	1447
BY97-5305C	530.5	2.8	-0.4	0.58	93	61	842
BY97-5579	557.9	2.6	0.6	0.59	112	61	3506
BY97-5694	569.4	1.8	-0.5	0.56	91	67	2298
BY97-5779	577.9	1.8	-0.7	0.55	121	131	2283
BY97-5874	587.4	2.3	0.3	0.54	165	108	1857
BY97-5939	593.9	1.6	0.2	0.58	104	189	5497
BY97-6022	602.2	1.8	-0.3	0.57	114	107	3879
BY97-6087A	608.7	1.8	-0.9	0.57	85	124	2152
BY97-6087B	608.7	1.9	-1.4	0.58	82	107	1729
BY97-6147	614.7	1.7	0.1	0.58	110	122	4198
BY97-6269	626.9	1.5	-1.1	0.59	101	84	2806
BY97-6350	635.0	0.9	-1.3	0.57	84	101	1716
BY97-6439	643.9	1.6	-1.5	0.59	89	72	1460
BY97-6567	656.7	1.8	-0.6	0.60	94	209	10185
BY97-6641	664.1	1.9	-0.4	0.59	105	108	2392
BY97-6741	674.1	1.4	-0.4	0.55	86	151	2911
BY97-6885A	688.5	1.7	-0.6	0.58	85	218	6679
BY97-6885B	688.5	1.9	-0.4	0.56	82	207	4986
BY97-6915A	691.5	1.8	0.5	0.56	99	258	2647
BY97-6915B	691.5	1.8	0.5	0.58	293	319	5294
BY97-7031	703.1	1.9	-0.8	0.57	88	211	6386
BY97-7087	708.7	2.7	-0.3	0.59	86	288	11027
BY97-7128	712.8	2.5	-1.7	0.56	59	121	2407
BY97-7382	738.2	1.9	-0.3	0.59	60	208	2104
BY97-8201	820.1	2.0	-1.3	0.55	69	416	6241
BY97-8261	826.1	1.7	-3.0	0.60	67	622	12927
BY97-8376	837.6	2.2	-1.3	0.56	72	240	4603
BY97-8570	857.0	2.0	-2.8	0.58	59	338	7015
BY97-8625	862.5	2.2	-0.6	0.57	55	305	6631

^a Calcitic samples are denoted by *; all other samples are dolomitic.

and 4 in Kah et al., 1999). Interpretation of isotopic and elemental trends are detailed in Kah et al. (1999), Kah (2000) and summarized here. Strontium content of marine carbonate rocks (normally > 1000 ppm) typically undergoes rapid depletion during diagenesis (Brand and Veizer, 1980). Sr contents of Bylot Island carbonates range from 1100 to 1400 ppm for limestone, and from 31 to 721 ppm for dolostone samples. Although low Sr contents may reflect dissolution-reprecipitation reactions in the presence of hybrid or non-marine waters, low Sr contents (typically 25–250 ppm) reported from dolomitic lithologies may simply reflect the dolomitization process, which preferentially excludes Sr from lattice substitution sites

(Sathyanarayan et al., 1987; Carpenter et al., 1991). ⁸⁷Sr/⁸⁶Sr ratios of dolomitic lithologies may therefore more closely reflect the composition of diagenetic fluids than do coeval limestones. Coeval limestone and dolostone samples from the Society Cliffs inner ramp on Baffin Island, however, have similar ⁸⁷Sr/⁸⁶Sr compositions consistent with reported values for late Mesoproterozoic seawater (Bartley et al., 2001), thereby suggesting that little non-marine fluid was involved in Society Cliffs diagenesis (Kah, 2000). In the absence of significant postdepositional meteoric diagenesis, correlation between enhanced Mn content (58–605 ppm) and low Sr abundance (Fig. 4(A)) may reflect the presence and activity of Mn-reducing bacteria

Table 2
Gypsum and pyrite isotopic and elemental compositions, Bylot Island

Sample ^a	Height (m)	$\delta^{34}\text{S}$ (‰ VCDT)	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppm)	Sr/Ca $\times 10^{-4}$ (mol/mol)	Na/Ca $\times 10^{-4}$ (mol/mol)	K/Ca $\times 10^{-4}$ (mol/mol)	Mg/Ca $\times 10^{-4}$ (mol/mol)
BY97-59	5.9	22.5	0.70580	961	15.0	1.5	0.9	32.7
BY97-96	9.6	22.6	0.70594	292	4.6	1.3	0.8	62.2
BY97-223	22.3	22.5	0.70665	2062	32.3	1.5	1.6	37.2
BY97-238	23.8	22.5	0.70777	1505	23.5	2.0	1.1	2.5
BY97-290	29.0	22.8	0.70578	2080	33.1	7.2	3.5	261.6
BY97-426	42.6	23.0	0.70607	1760	27.5	3.6	1.5	9.6
BY97-597	59.7	23.6	0.70575	1048	16.4	2.0	1.4	38.7
BY97-658	65.8	24.1	0.70542	1422	22.4	2.2	1.4	136.6
BY97-664	66.4	24.4	0.70540	1515	23.6	3.0	0.4	0.0
BY97-946	94.6	24.9	0.70565	1044	16.5	1.9	1.9	228.1
BY97-998	99.8	25.0	0.70548	1417	22.2	1.6	1.1	90.8
BY97-1231	123.1	25.2	0.70554	1618	25.9	2.3	2.3	399.1
BY97-1237	123.6	25.5	0.70573	1698	26.5	1.3	0.9	17.3
BY97-1337	133.7	25.0	0.70557	1549	24.6	3.7	4.0	287.5
BY97-1422	142.2	26.3	0.70587	1135	17.7	2.1	1.3	14.2
BY97-1554	155.4	26.2	0.70578	1415	22.2	1.7	1.5	112.9
BY97-1643	164.3	26.6	0.70612	1090	17.0	1.5	0.8	14.8
BY97-1731	173.1	27.1	0.70619	1055	16.6	1.4	1.5	140.5
BY97-2891	289.1	31.2	0.70677	1154	18.0	1.6	0.7	13.7
BY97-2910	291.0	30.6	0.70663	1238	19.3	1.4	0.8	0.0
BY97-2957	295.7	31.8	0.70659	1069	16.7	1.6	0.7	0.0
BY97-BY*	-20.0 ^b	4.5	—	—	—	—	—	—
BY97-BS182*	18.2	20.8	—	—	—	—	—	—
BY97-BS2784*	278.4	8.5	—	—	—	—	—	—
BY97-BS2806*	280.6	22.9	—	—	—	—	—	—
BY97-BS5145*	514.5	5.5	—	—	—	—	—	—
BY97-BS7098*	709.8	5.4	—	—	—	—	—	—

^a Pyritic samples are noted by *; all other samples are gypsum.

^b Arctic Bay Formation, estimated measurement from basal contact of the Society Cliffs Formation.

Table 3
Gypsum isotopic and elemental compositions, Baffin Island

Sample	Height (cm)	$\delta^{34}\text{S}$ (‰ VCDT)	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppm)	Sr/Ca $\times 10^{-4}$ (mol/mol)	Na/Ca $\times 10^{-4}$ (mol/mol)	K/Ca $\times 10^{-4}$ (mol/mol)	Mg/Ca $\times 10^{-4}$ (mol/mol)
TH97-G1	15.0	21.8	0.70610	2601	41.4	6.9	4.6	231.2
TH97-G2	30.0	22.9	0.70603	894	14.2	5.8	7.7	303.6
TH97-G3	45.0	23.0	0.70612	746	11.8	3.0	4.3	250.8
TH97-G4	60.0	23.1	0.70631	1349	21.2	3.6	3.6	94.5
TH97-G5	75.0	22.9	0.70637	1607	25.3	1.6	2.9	107.4
TH97-G6	90.0	22.5	0.70676	1194	18.8	1.6	2.5	116.3
TH97-G7	115.0	22.2	0.70706	516	8.3	4.3	2.4	556.4
TH97-G8	130.0	23.2	0.70703	1322	20.7	5.8	3.3	24.0
TH97-G9	145.0	23.3	0.70790	1050	16.4	1.4	1.4	41.5
TH97-3120	—	23.1	0.70768	884	14.3	4.4	20.3	519.9
TH97-3150	—	23.8	0.70647	1208	18.9	1.7	1.3	25.1
TH97-3720	—	23.5	0.70858	1063	16.6	2.4	1.9	41.4

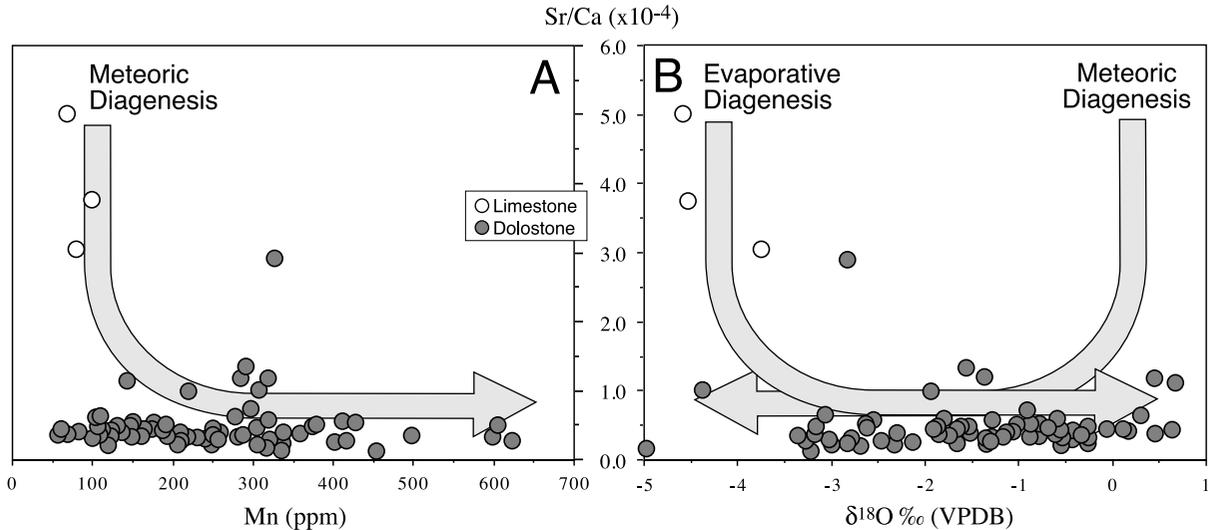


Fig. 4. Isotopic and elemental compositions of Society Cliffs carbonate rocks from Bylot Island. (A) Sr/Ca vs. Mn; (B) Sr/Ca vs. $\delta^{18}\text{O}$. Large arrow shows expected trends from precipitation or diagenesis in the presence of modified marine fluids (cf. Banner and Hanson, 1990). Open circles denote calcitic samples; filled circles denote dolomitic samples.

throughout carbonate deposition and early diagenesis (Hendry, 1993) of the Society Cliffs Formation.

Oxygen isotopic compositions of diagenetic carbonate lithologies provide valuable clues as to environments of diagenesis. Primary isotopic compositions are typically modified to reflect the isotopic composition of diagenetic fluids even at low water-rock ratios (Banner and Hanson, 1990). Although interpretation of ancient oxygen isotopic compositions is made difficult by ongoing controversy regarding the constancy of marine isotopic values through time (Knauth and Epstein, 1976; Muehlenbachs, 1986; Land and Lynch, 1996; Veizer et al., 1997; Kah, 2000; Frank and Lyons, 2000), diagenesis in the presence of fresh, meteoric, or connate fluids typically results in decreasing $\delta^{18}\text{O}$ with increasing diagenesis. Society Cliffs inner ramp carbonates, however, reveal isotopic values significantly heavier than values recorded from coeval mid-ramp open-marine environments (Kah, 2000), and a trend of increasing $\delta^{18}\text{O}$ with decreasing Sr/Ca (Fig. 4(B)). Together, these relationships are interpreted to reflect carbonate precipitation and early diagenetic dolomitization from isotopi-

cally depleted marine waters under increasingly evaporative conditions (see discussion in Kah, 2000).

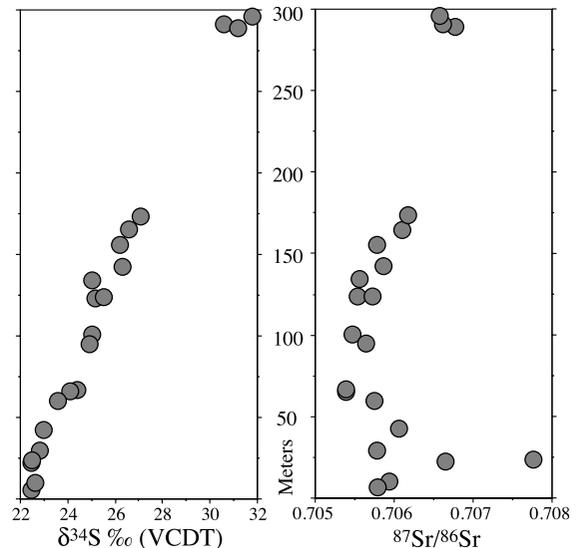


Fig. 5. Sulfur and strontium isotopic compositions of bedded gypsum from Bylot Island. $^{87}\text{Sr}/^{86}\text{Sr}$ shows the greatest variability $\sim 25\text{m}$ above the base of the Society Cliffs Formation, an interval of enhanced non-marine contribution to evaporative waters. See discussion in text.

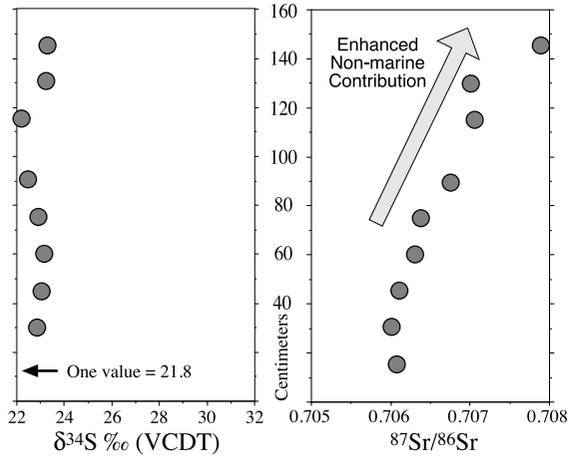


Fig. 6. Sulfur and strontium isotopic compositions of a single gypsum bed from Baffin Island, coeval with ~ 25 m interval on Bylot Island. Increasingly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values represent enhanced non-marine contribution to evaporative waters.

4.2. Interpretation of depositional and diagenetic trends of Society Cliffs gypsum

4.2.1. S isotope trends

Sulfur isotopic compositions of Society Cliffs gypsum range from $+21.8\text{‰}$ to $+31.8\text{‰}$ and show a near monotonic increase in isotopic composition with stratigraphic height (Tables 2 and 3; Fig. 5). Multiple samples measured both laterally and vertically within a single gypsum bed (samples BY97-223 and BY97-228 from Bylot Island, and samples TH97-1 through TH97-9 from Baffin Island; Figs. 5 and 6) reveal compositions that do not vary by more than 2‰ . Isotopic compositions of samples TH97-1 through TH97-9, all collected from a single 1.5 m thick gypsum bed on Baffin Island, closely correspond to the values reported by Olson (1984) from this same region (five samples, ranging from $+23.2\text{‰}$ to $+24.5\text{‰}$). Three lines of evidence, however, suggest that stratigraphic trends towards heavier $\delta^{34}\text{S}$ values record the temporal evolution of a regionally homogeneous parent brine: (1) individual gypsum beds do not vary in composition spatially, indicating a homogeneous parent fluid (cf. Nielsen, 1989; Leslie et al., 1997); (2) gypsum horizons occur only as restricted facies within 300 m of stacked carbon-

ate cycles, which are interpreted as recording repeated marine flooding (Kah, in press), thereby precluding gypsum formation during a single evaporative event; and (3) S isotopes within a single 1.5 m thick gypsum bed do not vary by more than 2‰ stratigraphically, suggesting basin inflow dominated primarily by a single parent brine (Claypool et al., 1980) and little evolution of parent brines via fractional crystallization during gypsum precipitation (Raab and Spiro, 1991).

It is more difficult to establish, however, whether increasingly enriched $\delta^{34}\text{S}$ compositions reflect basin-scale or global-scale compositional evolution of parent waters. Holser (1977) suggested that large brine-accumulating basins, limited in communication with the open ocean, could evolve highly enriched S-isotopic compositions, perhaps via biogenic H_2S reduction and large scale pyrite deposition within euxinic basinal brines (Leventhal, 1983), or via 'normal' sulfate reduction in a basin that is sulfate-limited from large scale deposition of evaporites (i.e. saline giants; Holser and Magaritz, 1987). Highly pyritic, organic-rich sediments are not preserved within the Society Cliffs basin and suggests that observed S isotope trends cannot be accounted for simply by high local rates of biogenic sulfate reduction. Furthermore, $\delta^{13}\text{C}$ values of Society Cliffs carbonates are typical of late Mesoproterozoic marine successions worldwide (Kah et al., 1999) and suggest that the Society Cliffs basin did not evolve extensively while isolated from a global marine reservoir.

Trends towards increasing S isotope enrichment in Society Cliffs gypsum are also strikingly similar to trends recorded in the Upper Marble of the similarly aged Grenville Supergroup (1270–1150 Ma; Friedman and Martignole, 1995). The Upper Marble consists of ~ 1000 m of dolomitic marble and quartzose dolomitic marble containing a variety of calc-silicate accessory minerals; anhydrite typically occurs as 1–15 m thick lenses and layers in the upper part of the unit (Whelan et al., 1990). Although metamorphism obscures many depositional features of the Upper Marble, Whelan et al. (1990) interpret deposition to have occurred in a marine setting based on the thickness and lateral extent of carbonate and evaporite facies, as well

as the C and O and $^{87}\text{Sr}/^{86}\text{Sr}$ (Hoff et al., 1984) isotopic compositions of carbonate facies. Within the Grenville Supergroup Upper Marble, Whelan et al. (1990) recorded stratigraphic variation in $\delta^{34}\text{S}$ of both anhydrite and disseminated pyrite within carbonate, similar in scale to that observed in the Society Cliffs Formation, (Fig. 7). Over an estimated stratigraphic interval of ~ 200 m, $\delta^{34}\text{S}$ of bedded anhydrite rises from values as low as $\sim +18\text{‰}$ to values near $+29\text{‰}$ before falling again to values near $+20\text{‰}$. Lower in the section, disseminated pyrite within dolomitic marble records a nearly 12‰ enrichment in ^{34}S (from 0‰ to $+12\text{‰}$) over ~ 200 m of section. Despite the absence of organic-rich/pyritic deposition within the basin, these trends were interpreted as reflecting rapid S-isotope evolution during extensive H_2S reduction in an enclosed, and therefore sulfate-limited basin (Whelan et al., 1990). Although coeval deposition of the Grenville and Bylot supergroups cannot presently be ascertained, we suggest that the marine character of carbonate lithologies, C-isotopic compositions, and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures precludes long-term isolation of these basins from the Mesoproterozoic global ocean. Furthermore, we suggest that the absence in either basin of highly pyritic or organic-rich deposition

coeval with carbonate and evaporite deposition, which would indicate significant local sulfate reduction, is consistent with the possibility that these large $\delta^{34}\text{S}$ fluctuations record true variation in the global marine sulfate reservoir.

4.2.2. Sr isotope trends

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Society Cliffs gypsum range from 0.70540 to 0.70858 (Tables 2 and 3). When examined within a stratigraphic context, $^{87}\text{Sr}/^{86}\text{Sr}$ declines from ~ 0.70600 to 0.70550 in the lower 100 m of the Society Cliffs Formation, followed by a gradual increase over the next 200 m to values near 0.70650 (Fig. 5). Variation to higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios occurs within a single 5 m stratigraphic interval ~ 25 m from the base of the section. On Bylot Island, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reach values of 0.70777 during this interval (Fig. 5), while climbing to values of 0.70858 over this same interval on Baffin Island (Fig. 6).

Sr isotopic compositions of marine minerals record the composition of parent fluids, which in turn reflect a complex interplay between hydrothermal alteration of young crustal basalts, typically at mid-ocean ridges, and fluvial input reflecting low-temperature alteration of old, continental crust (Peterman et al., 1970). Low $^{87}\text{Sr}/^{86}\text{Sr}$

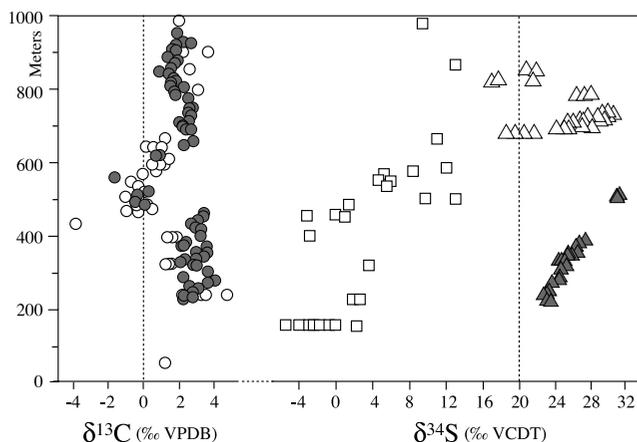


Fig. 7. Comparison of carbon and sulfur isotopic records from the Bylot and Grenville supergroups. Carbon isotopes from the Society Cliffs Formation, Bylot Island (filled circles) and the Upper Marble, Grenville Supergroup (open circles) show a strikingly similar pattern of mostly positive values near $+3\text{‰}$, with moderate variation to values near -1‰ . Sulfur isotopes from Society Cliffs gypsum (filled triangles) and Upper Marble anhydrite (open triangles) each reveal excursions of up to 15‰ over short stratigraphic intervals (~ 200 m). Upper Marble disseminated pyrite (open squares) show stratigraphic sulfur isotopic excursions of similar scale to those recorded in gypsum and anhydrite.

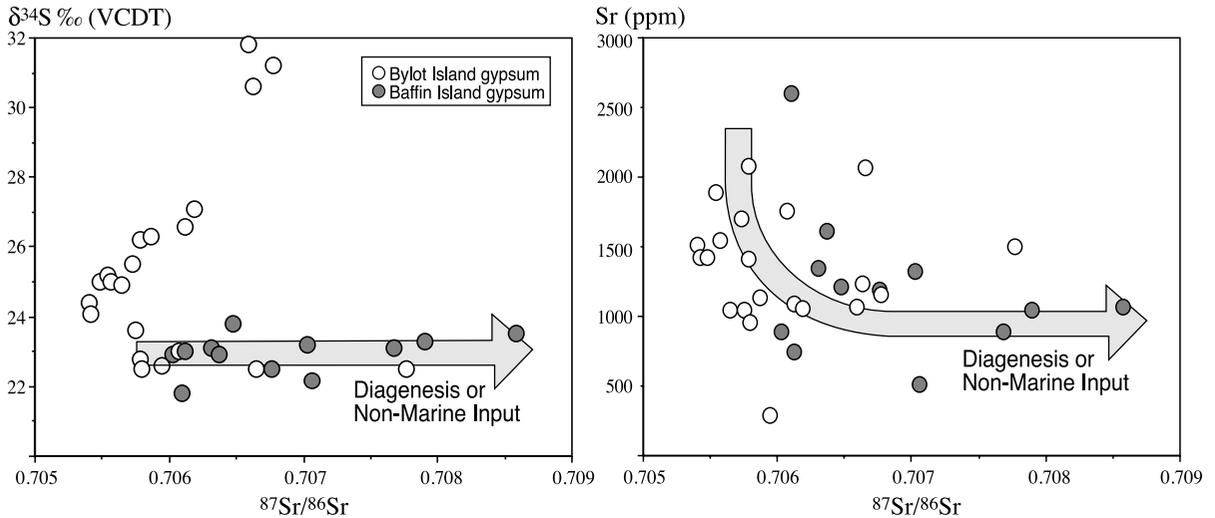


Fig. 8. Sulfur and strontium isotopic compositions of bedded gypsum from the Society Cliffs Formation, including samples collected from over 300 m of strata on Bylot Island (open circles) and samples from a 5 m thick interval on Baffin Island (filled circles). Large arrow shows expected trend from precipitation or diagenesis in the presence of marine waters modified by non-marine fluids (cf. Banner and Hanson, 1990).

ratios are therefore typically interpreted as recording times of enhanced circulation through mid-ocean ridges during periods of rapid crustal production (Veizer et al., 1982, 1983), whereas high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are thought to reflect greater input via weathering of older, terrestrial sources (Derry et al., 1992; Montañez et al., 1996). Because the residence time of Sr is long, and marine Sr isotopic composition is uniform, rapid variation in $^{87}\text{Sr}/^{86}\text{Sr}$ under the highly restricted conditions necessary for evaporite formation is typically interpreted to reflect regional modification of evaporative fluids from non-marine sources (Clauer, 1976; Chaudhuri and Rahman, 1987; Chaudhuri and Clauer, 1992).

At present, the dataset representing Mesoproterozoic marine $^{87}\text{Sr}/^{86}\text{Sr}$ is relatively small, consisting of several published values from carbonate rocks of the Belt Supergroup (Hall and Veizer, 1996), the Jixian System (Jahn and Cuvelier, 1994), and the Bylot Supergroup (Kah, 2000), as well as larger datasets from the Ural Mountains (Gorokhov et al., 1996) and the Turukhansk and Uchur-Maya successions of Siberia (Bartley et al., 2001, and references therein). Evaluation of these datasets indicate that late Mesoproterozoic

to early Neoproterozoic seawater fluctuated in composition between ~ 0.7053 and 0.7063 (Bartley et al., 2001). The majority of Society Cliffs gypsum samples record $^{87}\text{Sr}/^{86}\text{Sr}$ values within the range of inferred marine values and are consistent with values obtained from coeval Bylot Supergroup carbonates ($0.70518\text{--}0.70627$; Kah, 2000), indicating a dominantly seawater source for evaporative brines. The extent of non-marine fluid contribution to Society Cliffs gypsum necessary to attain measured deviations from marine compositions can be estimated from a simple mixing model (Chaudhuri and Clauer, 1992). Assuming an average marine $^{87}\text{Sr}/^{86}\text{Sr}$ composition from coeval carbonates (0.7060) and a non-marine component comparable to the average modern fluvial composition (0.7110 ; Wadleigh et al., 1985), the majority of Society Cliffs gypsum samples record minimal contribution from non-marine fluids ($< 10\%$).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios elevated from presumed coeval seawater occur within a single 5 m stratigraphic interval ~ 25 m from the base of the stratigraphic section (Fig. 8). Samples within this interval show both low Sr concentration and elevated $^{87}\text{Sr}/^{86}\text{Sr}$, suggesting significant contribution from non-

marine fluids during deposition or diagenesis (Fig. 8; Banner and Hanson, 1990; Banner, 1995). On Baffin Island this interval contains a 1.5 m thick gypsum bed composed of mm- to cm-scale laminae marked by increasing green shale content in the upper half of the section. Gypsum is overlain by a thick interval of red shale containing mud-cracks, current and wave ripples, and several more cm-thick gypsum horizons. S isotopic composition of gypsum throughout this interval remains constant within 2‰. Similarly, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain constant at ~ 0.70610 in the basal 40 cm of the thick gypsum bed, but quickly rise to 0.70790 at the contact with overlying shale (Fig. 6) and reach values of 0.70858 in gypsum within the overlying shale (Table 3). Mixing calculations indicate that, in the absence of detectable contamination from terrigenously derived ^{87}Rb , $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70858 require greater than 50% non-marine contribution to evaporative fluids. An interpretation of increasing non-marine influx to the basin during deposition of this gypsum interval is consistent with geologic evidence of increasing terrigenous shale influx. Direct correlation between geochemical signatures and observed depositional processes also suggests that Sr isotopic compositions remained buffered by gypsum during dehydration/rehydration reactions.

4.2.3. Composition of evaporative brines

Minor or trace elements can be incorporated by substitution into the gypsum lattice (McIntire, 1963), by charge-balanced electrostatic adsorption within hydration waters (Kushnir, 1980), or as fluid or solid inclusions (Lu et al., 1997). Of these, only direct lattice substitution accurately records brine compositions in ancient evaporites, which have commonly undergone dehydration and rehydration. Brine compositions can be calculated using partition coefficients derived experimentally, observationally, or thermodynamically; these are expressed via the relationship $D_x = [\text{X}/\text{Ca}_{\text{solid}}]/[\text{X}/\text{Ca}_{\text{brine}}]$, where X represents the concentration of the coprecipitated cation relative to Ca^{2+} in the mineral and its coexisting brine. Kushnir (1980, 1982) detailed the derivation of partition coefficients for the coprecipitation of Sr, Na, K, and Mg into gypsum and anhydrite. Coprecipitation

depends primarily on three parameters: temperature of precipitation, brine concentration, and kinetic effects associated with rates of crystal growth. D_x typically increases with brine concentration and growth rate. Increasing temperature, on the other hand, typically decreases D_x and subdues kinetic effects associated with growth rate. Additionally, D_x is quite small for Na, K and Mg, and the amount of coprecipitation has little effect on overall brine composition during precipitation at a constant degree of supersaturation. Sr, however, shows significantly greater coprecipitation, resulting in an overall depletion of brine Sr during continued mineral precipitation.

Table 4 contains measured concentrations of major ions during evaporation of modern seawater (Fontes and Matray, 1993), presented as molar ratios relative to Ca^{2+} ; calculated cation ratios of hypothetical gypsum precipitating from modern seawater saturated with respect to both gypsum and halite; and measured values from Society Cliffs gypsum. Partition coefficients for cation incorporation into gypsum are from Kushnir (1980)(Table 4). Measured cation ratios are also plotted with respect to stratigraphic position for Bylot (Fig. 9) and Baffin (Fig. 10) Island evaporites. Overall, ratios of major cations in Society Cliffs gypsum ($\text{Sr}/\text{Ca}_{\text{ave}} = 0.00212$; $\text{K}/\text{Ca}_{\text{ave}} = 0.00014$) are strikingly similar to expected compositions of CaSO_4 forming from modern seawater at gypsum saturation ($\text{Sr}/\text{Ca}_{\text{ave}} = 0.00274$; $\text{K}/\text{Ca}_{\text{ave}} = 0.00017$). Ba concentrations (0–35 ppm, unpublished data) are also within the range of Phanerozoic marine gypsum samples (Spötl and Pak, 1996; Leslie et al., 1997), although the partition coefficient for Ba incorporation into CaSO_4 evaporites is not known. Na/Ca ratios (in the range of 0.00025), however, are significantly depleted relative to expected values ($\text{Na}/\text{Ca}_{\text{ave}} = 0.00685$), and Mg/Ca ratios of ~ 0.00876 are significantly enriched with respect to expected values ($\text{Mg}/\text{Ca}_{\text{ave}} = 0.00011$). In all cases, cation ratios reveal significant enrichment at 25 and 125 m (Fig. 9).

Because the concentration of major seawater cations generally increases with increasing salinity, enrichment of measured cation ratios at 25 and 125 m (Fig. 9) most likely reflects increased

Table 4

Cation ratios of modern seawater brines, and projected and measured CaSO_4 compositions

Ratio	Seawater (mol/mol) ^f	Gypsum (mol/mol) ^f	Halite (mol/mol) ^f	X/Ca CaSO_4 (gypsum sat.)	X/Ca CaSO_4 (halite sat.)	X/Ca CaSO_4 (Bylot Island)
Sr/Ca	0.0089	0.0066	0.0363	0.00099 ^a	0.00544 ^a	0.00046 ^c
				0.00449 ^b	0.02468 ^b	0.00331 ^d
				0.00274 ^c	0.01506 ^c	0.00212 ^c
Na/Ca ^g	45.660	42.792	368.43	0.00043 ^a	0.00368 ^a	0.00013 ^c
				0.01327 ^b	0.11421 ^b	0.00078 ^d
				0.00685 ^c	0.05895 ^c	0.00025 ^c
K/Ca	0.9958	0.9785	8.2005	0.00001 ^a	0.00008 ^a	0.00004 ^c
				0.00033 ^b	0.00279 ^b	0.00040 ^d
				0.00017 ^c	0.00144 ^c	0.00014 ^c
Mg/Ca	5.1827	4.8508	49.1049	0.00001 ^a	0.00005 ^a	0.00000 ^c
				0.00021 ^b	0.00211 ^b	0.03371 ^d
				0.00011 ^c	0.00108 ^c	0.00876 ^c

^a Calculated from low estimated distribution coefficients Sr = 0.15, Na = 0.00001, K = 0.00001, Mg = 0.000001.^b Calculated from high estimated distribution coefficients Sr = 0.68, Na = 0.00031, K = 0.00034, Mg = 0.000043.^c Lowest measured value from Bylot Island section.^d Highest measured value from Bylot Island section.^e Average calculated and measured values.^f Evolved water compositions from Fontes and Matray (1993); distribution coefficients from Kushnir (1980).^g Lu et al. (1997) suggest currently accepted Dna(gypsum) values may be up to two orders of magnitude too high.

evaporation during these intervals. Similarly, variable cation ratios from within a single gypsum interval from Baffin Island (Fig. 10) can best be viewed as reflecting fluctuating concentration of

evaporative fluids in combination with increased fluid contribution from non-marine sources, as indicated by increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This interpretation, however, does not address the overall

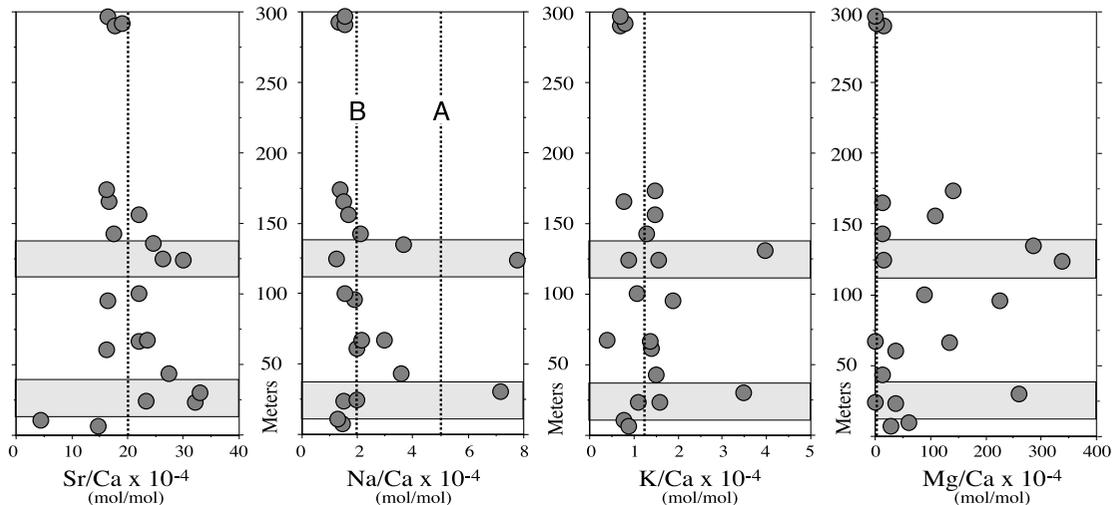


Fig. 9. Elemental analyses (Sr, Na, K, Mg) of Bylot Island gypsum presented as molar ratios with respect to Ca. Dotted lines represent molar ratios calculated for gypsum precipitating from modern seawater at gypsum saturation, based on distribution coefficients of Kushnir (1980). Line A for Na/Ca ratios represents distribution coefficient of Kushnir (1980), Line B represents revised distribution coefficients based on estimates of Lu et al. (1997).

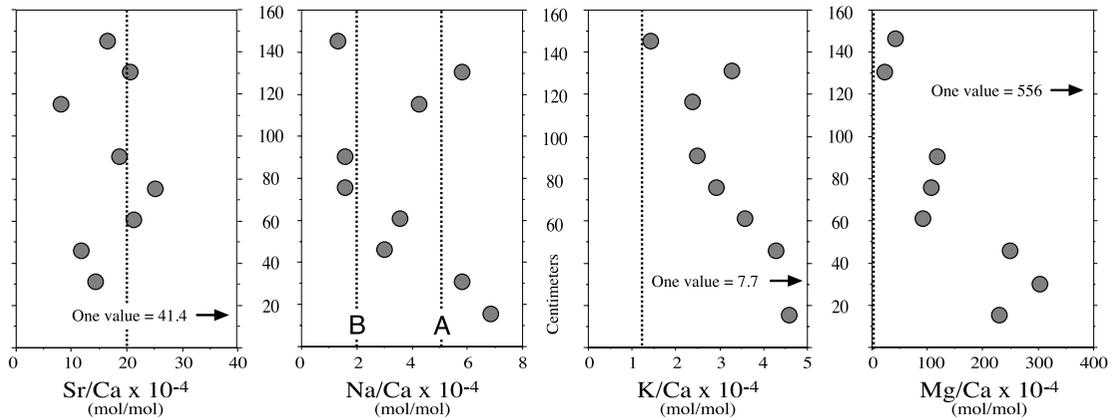


Fig. 10. Elemental analyses (Sr, Na, K, Mg) of a single gypsum bed from Baffin Island, presented as molar ratios with respect to Ca. Dotted lines, as in Fig. 7, represent molar ratios calculated for gypsum precipitating from modern seawater at gypsum saturation, based on distribution coefficients of Kushnir (1980) and estimated of Lu et al. (1997). Generally decreasing elemental concentrations support $^{87}\text{Sr}/^{86}\text{Sr}$ values indicating an upsection increase in the contribution of non-marine fluids.

depletion of Na/Ca and enrichment of Mg/Ca. Diagenetic effects, such as those that occur during dissolution-precipitation reactions during gypsum dehydration and rehydration may, of course, affect mineral compositions. The similarity of gypsum and anhydrite distribution coefficients, however, indicates that when dehydration/rehydration reactions occur in pore fluids of low ionic strength, composition of resulting minerals will be controlled predominantly by the composition of the parent material (Kushnir, 1980). Only in the presence of volumetrically significant fluid inclusions or very concentrated pore waters will resulting mineral phases differ significantly in composition from the parent phase. For cation ratios in Society Cliffs gypsum to reflect a diagenetic component imparted during dehydration-rehydration, requisite brines must be enriched in SO_4^{2-} , Mg^{2+} , and K^+ , and depleted in Na^+ . Mg^{2+} enrichment is common in non-marine and hydrothermal brines, and such brines cannot be ruled out. However, Na^+ depletion is not generally typical of non-marine, meteoric, or hydrothermal brines (Eugster and Hardie, 1978; Hardie, 1984, 1991) and, in the case of the Society Cliffs Formation, $^{87}\text{Sr}/^{86}\text{Sr}$ appears to faithfully record local marine compositions.

Na^+ depletion in Society Cliffs gypsum is perhaps better explained by an overestimation of

current partition coefficients. Lu et al. (1997) found that when evaporite samples were powdered and subjected to an alcohol rinse and HNO_3 treatment to remove both fluid and solid inclusions prior to dissolution and trace element analysis, Na^+ concentrations were lowered by one to two orders of magnitude. Society Cliffs samples were subjected to an alcohol rinse and are believed to contain minimal contamination from fluid or solid inclusions. If Lu et al. (1997) are correct, apparent Na^+ depletion observed in Society Cliffs gypsum may be consistent, in fact, with gypsum precipitation from brines similar to modern seawater at or near gypsum saturation. However, this model cannot account for significantly enriched Mg^{2+} contents of Society Cliffs gypsum. In the absence of contamination from late-stage evaporative fluid inclusions (e.g., carnallite, which would release Mg^{2+} upon dehydration conversion to sylvite; Warren, 1996) or solid, presumably dolomitic, inclusions, Mg/Ca enrichments in Society Cliffs gypsum may best be interpreted as reflecting true variation in marine Mg/Ca composition during evaporite precipitation.

4.2.4. Interpretation of Mesoproterozoic marine sulfate compositions

Constraints from stratigraphy, composition of associated lithologies, isotopic and elemental com-

positions of associated carbonates, Sr isotopes, and cation ratios (Sr/Ca, Na/Ca, K/Ca) all suggest a predominantly marine origin for Society Cliffs gypsum. The preserved upsection shift in $\delta^{34}\text{S}_{\text{sulfate}}$ from $\sim +22\text{‰}$ to $+32\text{‰}$ is therefore interpreted as recording primary variation in marine sulfate compositions. Similar isotopic trends recorded in late Mesoproterozoic evaporites of the Grenville Supergroup (Whelan et al., 1990) suggest that such large isotopic fluctuations may be common occurrences in Mesoproterozoic marine waters.

Although large fluctuations in the S isotopic composition of marine waters have occurred at numerous times during the Phanerozoic (Claypool et al., 1980), these fluctuations have typically occurred over much longer time-scales and have largely been compensated by a decrease in seawater $\delta^{13}\text{C}$ (Holser, 1984). This broad inverse correlation between C and S isotopes is interpreted as the primary evidence for a steady-state environmental linkage between reduced and oxidized C and S (and Fe) reservoirs during the Phanerozoic, which has helped maintain atmospheric pO_2 within a relatively narrow window (Holland, 1973; Garrels and Perry, 1974; Schidlowski et al., 1977; Veizer et al., 1980; Berner and Raiswell, 1983; Holser, 1984; Carpenter and Lohmann,

1997; Canfield, 1998). It has also been suggested that biospheric C–S linkages were operating in the Neoproterozoic as well, though perhaps modified by the presence of lower atmospheric pO_2 (Strauss, 1993; Carpenter and Lohmann, 1997).

The large isotopic variation recorded here and in the Grenville Supergroup (Whelan et al., 1990), however, occurs over only a few hundred meters and without a corresponding decrease in $\delta^{13}\text{C}$ (Fig. 11). Many Neoproterozoic evaporite sequences also show a similar range and/or stratigraphic variation in $\delta^{34}\text{S}$, without a corresponding decrease in $\delta^{13}\text{C}$ (Strauss, 1993; Walter et al., 2000; and references therein). If occurring within a global marine reservoir, these large, rapid isotopic shifts must, instead, be interpreted as reflecting non-steady state conditions (Holser, 1977) or small-scale variation not balanced by the exogenic system (Nielsen, 1989; Holser et al., 1989; Paytan et al., 1998). The lack of correlation between C and S isotopes in the Bylot and Grenville supergroups is not surprising; response times of these isotopic systems are strongly influenced by their respective residence times in the ocean (Veizer et al., 1999) and correlation is typically observed on time scales > 50 Ma (Holser, 1984). Estimates of deposition rate suggest that evaporite-rich inter-

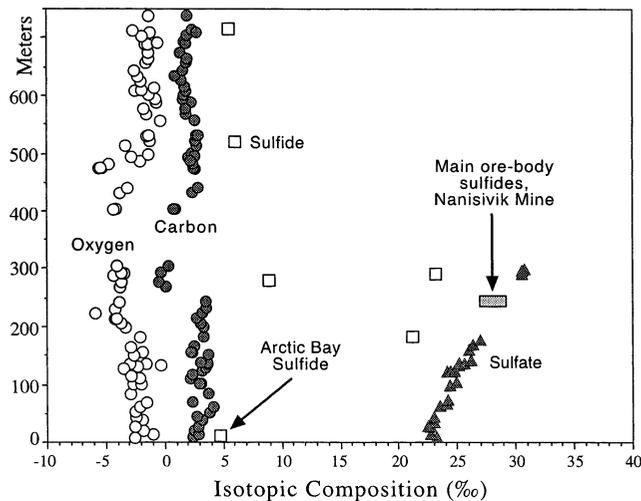


Fig. 11. Summary of isotopic data from the Society Cliffs Formation on Bylot Island, including $\delta^{13}\text{C}$ (filled circles), $\delta^{18}\text{O}$ (open circles), $\delta^{34}\text{S}_{\text{sulfate}}$ (filled triangles), and $\delta^{34}\text{S}_{\text{sulfide}}$ (open squares). Heavy $\delta^{34}\text{S}_{\text{sulfide}}$ values of Nanisivik Mine ore-stage pyrites are from Ghazban et al. (1990), who interpreted values as representing complete in situ reduction of seawater sulfate from pore fluids.

vals of the Society Cliffs Formation and Upper Marble, Grenville Supergroup, record isotopic variation occurring on time scales <20 Ma. However, in the modern ocean, carbon isotopes typically respond on much shorter time scales than do sulfur isotopes. More rapid S-isotopic variation in these units suggests, therefore, that the Mesoproterozoic marine sulfate reservoir may have been significantly smaller than that of the present ocean. Reduction in size of the marine sulfate reservoir, perhaps imposed by reduced biospheric oxygen levels, may have resulted in a greater sensitivity in response to variation imposed by C–S–Fe redox cycling (Canfield, 1998), ultimately leading to rapid fluctuations in the isotopic composition of the marine sulfate reservoir. Short-term decoupling of the exogenic C–S system may have also been accentuated by higher total dissolved inorganic carbon (DIC) in the Precambrian (Grotzinger and Kasting, 1993), which may have buffered marine inorganic C isotopic compositions to such an extent as to render modest variation resulting from C–S–Fe redox cycling unmeasurable.

4.3. Isotopic composition of Society Cliffs sulfides

Eighteen samples of black shale and shaly carbonate from the Society Cliffs Formation were analyzed for total C_{org} and S_{pyrite} . The relationship between C_{org} and S_{pyrite} in sedimentary systems has been demonstrated to be a powerful tool for interpreting normal marine, fresh- to brackish, and euxinic depositional paleoenvironments, and have been successfully applied to Precambrian systems (Berner, 1982; Lyons et al., 2000). Under normal marine conditions, the supply of sulfate is not limiting and, given sufficient C_{org} , considerable bacterial sulfate reduction and pyrite formation can occur. In contrast, many euxinic environments show decoupling within the C–S system and may have substantial pyrite accumulation despite lower C_{org} (Lyons and Berner, 1992), and fresh to brackish environments show limited sulfate availability despite high C_{org} contents (Berner and Raiswell, 1983). Unfortunately, generally low abundance of both C_{org} (0.00–2.67 wt.%, 0.17 median wt.%) and S_{pyrite} (0.02–1.22

wt.%, 0.06 median wt.%) in Society Cliffs samples are non-diagnostic with respect to paleoenvironmental models. However, isotopic compositions of carbonate (C, O, Sr) and gypsum (Sr) suggest a dominantly marine, rather than fresh- or brackish-water source for the basin, and low C_{org} values in this case most likely reflect the high carbonate content of samples. C_{org} production and subsequent bacterial activity and S_{pyrite} formation may have also been inhibited by the extreme hypersaline conditions represented in this section (Javor, 1989).

Five shale samples with wt.% $S_{pyrite} > 0.1\%$ were analyzed for S-isotopes. These included two samples from within the lower 300 m (evaporite-bearing) of the Society Cliffs Formation, two samples from overlying Society Cliffs strata, and one from the underlying Arctic Bay Formation. Black shale of the Arctic Bay Formation has been interpreted as open marine in origin (Jackson and Iannelli, 1981) and should therefore constrain bacterial sulfate reduction in unrestricted marine conditions. S isotopic compositions of Society Cliffs sedimentary sulfides range from +5.4‰ to +22.9‰, with the single Arctic Bay sample recording a value of +4.5‰ (Table 2; Fig. 10). Heavy $\delta^{34}S$ values for Society Cliffs sulfides are similar to ^{34}S -enriched values obtained from ore-stage pyrites (from +21‰ to +31‰) within the western Bylot basin (Olson, 1984; Ghazban et al., 1990), which have been interpreted to reflect nearly complete in situ bacterial reduction of a limited seawater sulfate source (Ghazban et al., 1990). Such enriched $\delta^{34}S_{sulfide}$ values are not uncommon in Mesoproterozoic and Neoproterozoic marine successions (Burnie et al., 1972; Lambert, 1984; Whelan et al., 1990; Bottomley et al., 1992; Ross et al., 1995; Canfield and Teske, 1996; Strauss, 1997; Logan et al., 1999; Lyons et al., 2000; Luepke and Lyons, 2001). Sulfate limitation, and resultant enriched $\delta^{34}S_{sulfide}$ values, can be reached locally whenever the rate of sulfate consumption approaches or exceeds the rate of sulfate supply (Chambers and Trudinger, 1979; Ohmoto and Felder, 1987; Zaback et al., 1993). Because Precambrian sediments lack bioturbation and sulfate supply to pore waters is diffusion controlled, enriched $\delta^{34}S_{sulfide}$ values likely reflect

pore-water modification during ongoing sulfate reduction, perhaps accentuated by the presence of a global marine sulfate reservoir that may have been significantly smaller than at present.

5. Implications for ocean-atmosphere evolution

5.1. C–S systematics and Proterozoic biospheric evolution

The linkage between carbon and sulfur isotope systems and the Earth's biospheric evolution have been reviewed in detail in a number of publications (Holland, 1973; Veizer et al., 1980; Holser et al., 1988, 1989; Schidlowski, 1989; Strauss, 1993, 1997; Veizer et al., 1999) and will only be summarized here. From a geologic perspective, marine carbon and sulfur reside in the biosphere as both oxidized and reduced species, with the reduced species formed via biological activity. These biochemical reduction processes (i.e. photosynthetic production of organic matter and bacterial sulfate reduction) produce large isotopic fractionations, which leave oxidized reservoirs isotopically enriched and reduced reservoirs isotopically depleted with respect to ^{13}C and ^{34}S . As a result of these fractionation mechanisms, the balance between oxidized and reduced species in the marine system is reflected by variation in the isotopic composition of complementary oxidized and reduced carbon and sulfur reservoirs through time.

In the modern highly oxygenated open-marine system – in which biological reduction processes are limited with respect to neither dissolved carbon dioxide nor dissolved sulfate – C and S isotope systems are broadly linked via a complex set of feedbacks, resulting in an inverse correlation between the isotopic composition of oxidized reservoirs (Berner and Petsch, 1998; Berner, 1999). In the broadest sense, increased burial of photosynthetically produced organic carbon results in an increase in the isotopic composition of oxidized carbon reservoirs and a release of oxygen to the biosphere, which is balanced by the oxidation of reduced sulfur species. In contrast, the Proterozoic biosphere contained, at maximum, less than 10–20% of present-day oxygen levels

(Berkner and Marshall, 1965; Runnegar, 1982; Knoll, 1992), resulting in a modified marine C–S cycle in which S isotope variation was dominantly controlled by marine sulfate availability (Chambers and Trudinger, 1979; Strauss, 1993). Total fractionation ($\Delta^{34}\text{S}$) between oxidized and reduced forms reflects the maximum fractionation ($\Delta^{34}\text{S}_{\text{max}}$) induced by bacterial sulfate reduction when the system is non-limiting with respect to sulfate availability. Similarly, if $\Delta^{34}\text{S} < \Delta^{34}\text{S}_{\text{max}}$, then conditions are limited with respect to sulfate, in which case progressive reduction of sulfate will continue to modify the isotopic composition of the sulfate reservoir until the isotopic compositions of complementary oxidized and reduced reservoirs converge (Chambers and Trudinger, 1979).

In light of this relationship, an observed $\Delta^{34}\text{S}_{\text{max}}$ of $\sim 0\text{‰}$ in Archean and Paleoproterozoic marine systems (Strauss, 1993, and references therein) is interpreted to reflect extreme sulfate limitation in a largely reducing early Earth biosphere (for alternate view see Ohmoto and Felder, 1987; Ohmoto et al., 1993). Following an organic carbon burial event and corresponding oxygenation event between ~ 2.2 and 1.9 Ga, as manifested in $\delta^{13}\text{C}$ records (Des Marais et al., 1992; Karhu and Holland, 1996), increased concentrations of marine sulfate are recorded in the geologic record as a greater fractionation expressed by biological sulfate reduction (Habicht and Canfield, 1996), and a resulting increase in $\Delta^{34}\text{S}_{\text{max}}$ to $\sim 25\text{--}30\text{‰}$ (Cameron, 1982; Strauss, 1993, and references therein; Canfield, 1998). Similarly, a further increase in $\Delta^{34}\text{S}_{\text{max}}$ to $> 40\text{‰}$, recorded in Neoproterozoic rocks (Strauss, 1993, and references therein), is interpreted to record a significant increase in the marine sulfate reservoir size (Canfield and Teske, 1996; Canfield, 1998) following a second major organic carbon burial event (Knoll et al., 1986; Des Marais et al., 1992).

5.2. Mesoproterozoic biospheric evolution

5.2.1. A Mesoproterozoic oxygenation event

As outlined above, investigations into Precambrian biospheric evolution have largely focused on the interval prior to and between ~ 2.2 and 1.9

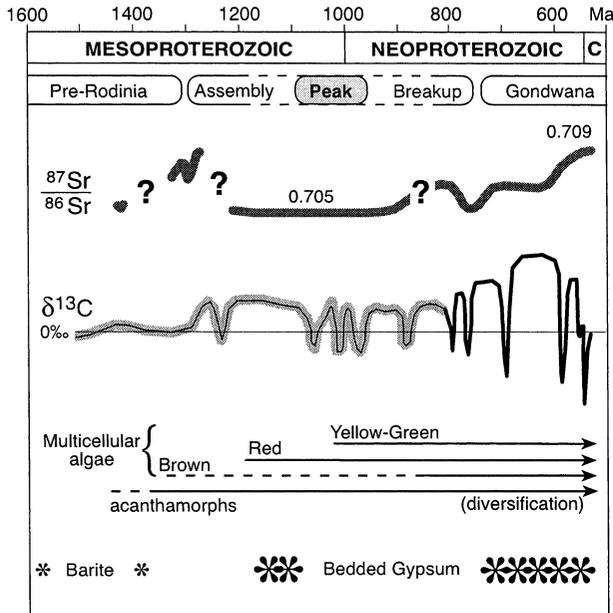


Fig. 12. Summary of biogeochemical events in the Mesoproterozoic and Neoproterozoic. Arc formation at the margins of Laurentia at ~ 1300 Ma (McLelland et al., 1996) marks the beginnings of protracted assembly of Rodinia, which peaked asynchronously between ~ 1100 and 960 Ma (McLelland et al., 1996; Martignole and Friedman, 1998). Elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values, consistent with an increased continental input of Sr to seawater, correspond with the initial stages of Rodinia assembly (Bartley et al., 2001). Enhanced sedimentation and C_{org} burial at this time may also have resulted in a first-order shift in the carbon isotopic composition of the oceans from values near 0‰ to moderately positive values near $+3.5\text{‰}$ (Kah et al., 1999). Elevated $\delta^{13}\text{C}$ compositions may be with Proterozoic oxygenation events (Knoll, 1992; Des Marais et al., 1992; Karhu and Holland, 1996), which may be recorded in the Mesoproterozoic by the appearance of distinct acanthomorphic acritarchs (Xiao et al., 1997), the evolution of early multicellular algal lineages (Woods et al., 1998; Butterfield, 2001), and the appearance of laterally extensive, bedded gypsum. Sulfate deposition prior to ~ 1.3 Ga is limited to barite occurrences in the Belt and McArthur supergroups. See discussion and references in text.

Ga, during which the Earth's biosphere is believed to have first experienced significant oxygenation (Walker et al., 1983; Holland and Beukes, 1990; Karhu and Holland, 1996; Sumner and Grotzinger, 1996a,b; Sumner, 1997; Rye and Holland, 1998; Melezhik et al., 1999; Canfield et al., 2000); and the later Neoproterozoic (< 850 Ma), at which point oxygenation of the Earth's bio-

sphere is believed to have reached levels sufficient to support the earliest metazoan life (Runnegar, 1982; Knoll, 1992; Brasier et al., 1996; Hoffman et al., 1998; Knoll and Carroll, 1999; Walter et al., 2000). Research conducted in the past five years, however, has increased our knowledge of biospheric evolution during the Mesoproterozoic Era as well (Fig. 12). The Mesoproterozoic, rather than representing 'the duller time in Earth history' (Buick et al., 1995), or recording 'a billion years of environmental stability' (Brasier and Lindsay, 1998), now appears to represent a critical interval in the oceans with respect to changing carbonate saturation (Kah and Knoll, 1996; James et al., 1998; Bartley et al., 2000; Sherman et al., 2000; Kah, in press), diversification of complex unicellular eukaryotes (Xiao et al., 1997), and the evolution and diversification of multicellular algal life (Butterfield et al., 1990; Woods et al., 1998; Butterfield, 2001).

Furthermore, the emerging carbon isotope record reveals that a first-order, $3\text{--}4\text{‰}$ shift in $\delta^{13}\text{C}$ in the world's oceans occurred in the latter half of the Mesoproterozoic (Knoll et al., 1995; Kah et al., 1999; Bartley et al., 2001) between ~ 1.3 and 1.25 Ma. During this short time interval, the overall carbon isotopic composition of the ocean changed from $\sim 0\text{‰}$, where it had remained for some 700 million years (Lindsay and Brasier, 2000), to $\sim +4.0\text{‰}$, where, despite transient fluctuations, it remained until rising to even higher values in the later Neoproterozoic (Kah et al., 1999; Bartley et al., 2001). This single positive carbon isotope event, though moderate in magnitude when compared to isotopic shifts of up to 10‰ in the latest Neoproterozoic (Kaufman and Knoll, 1995), is as great as the largest changes observed in Phanerozoic seawater (Holser, 1984; Veizer et al., 1999) and suggests a fundamental modification of the biogeochemical carbon cycle. Interpretation of C and Sr isotopic records over this interval suggests that increased sedimentation rates associated with initial assembly of Rodinia may have resulted in increased organic carbon burial fluxes, thereby triggering the observed change in Mesoproterozoic $\delta^{13}\text{C}$ (Bartley et al., 2001). Linkages between organic carbon burial and biospheric oxidation (Holland, 1973; Garrels

and Perry, 1974; Schidlowski et al., 1975; Veizer et al., 1980; Berner, 1987; Des Marais et al., 1992), in turn, suggest that the observed Mesoproterozoic carbon burial event should correspond to a global biospheric oxygenation event. If the observed carbon isotope shift heralds a change in the oxygenation of the ocean-atmosphere system, increased O₂ availability may have been a factor in the near simultaneous appearance of bedded sulfates (Grotzinger, 1994) and origin of multicellularity (Butterfield et al., 1990; Woods et al., 1998; Butterfield, 2001). Furthermore, because the carbon and sulfur cycles are linked via redox potential, the hypothesis of increased oxidation should be testable by examining the geologic record of sulfur during this interval.

5.2.2. A test of ocean-atmosphere oxygenation

Canfield and Teske (1996) suggested, based on a temporal correlation of an apparent increase in $\Delta^{34}\text{S}_{\text{max}}$ from $\sim 25\text{--}30\text{‰}$ to $> 40\text{‰}$ and a proposed evolutionary event inferred from 18s rRNA sequence data, that the Neoproterozoic marks a significant change in the composition of biogenic sulfur-metabolizing communities. They suggested that prior to ~ 850 Ma, oxygen-poor marine environments were incapable of supporting a modern complement of sulfur metabolizing bacteria and that sulfur metabolizing communities lacked the critical membership of colorless sulfur oxidizing bacteria, which require a threshold of free oxygen in the environment for their metabolism (Jørgensen, 1983), and are critical in performing a sulfur disproportionation step necessary to achieve modern magnitudes of $\Delta^{34}\text{S}_{\text{max}}$. In the absence of this sulfur disproportionation step, Canfield and Teske (1996) hypothesized that $\Delta^{34}\text{S}_{\text{max}}$ achievable by a more primitive community of sulfur metabolizing bacteria could not have exceeded $25\text{--}30\text{‰}$, reflecting the maximum kinetic isotope fractionation during bacterial sulfate reduction in the absence of S disproportionation during redox cycling (Canfield and Thamdrup, 1994).

The scenario outlined by Canfield and Teske (1996) provides a framework for examining the hypothesis of a Mesoproterozoic rise in biospheric oxygen (Kah et al., 1999). If Canfield and Teske are incorrect in their suggestion that a modern sulfur-

metabolizing community capable of achieving $\Delta^{34}\text{S}_{\text{max}} > 40\text{‰}$ did not evolve until ~ 850 Ma, then observed early Mesoproterozoic $\Delta^{34}\text{S}_{\text{max}}$ of $25\text{--}30\text{‰}$ must reflect oxygen-controlled sulfate limitation. A Mesoproterozoic oxygenation event, therefore, should result in a concomitant increase in $\Delta^{34}\text{S}_{\text{max}}$ as sulfate limitation is reduced with increased biospheric oxygen and a concomitant increase in the marine sulfate reservoir size. If, on the other hand, Canfield and Teske (1996) are correct that the observed increase in total range of $\delta^{34}\text{S}_{\text{pyrite}}$ reflects a true increase in $\Delta^{34}\text{S}_{\text{max}}$ due to Neoproterozoic evolutionary innovations, then $\Delta^{34}\text{S}_{\text{max}}$ in the Mesoproterozoic would be expected to reflect the hypothetical $\Delta^{34}\text{S}_{\text{max}}$ of $25\text{--}30\text{‰}$, regardless of fluctuations in pO₂. In this case, S-isotopic compositions would not be expected to resolve the hypothesized linkage between Mesoproterozoic oxygenation and an increase in the size of the marine sulfate reservoir.

Data obtained from sedimentary pyrite (Strauss and Schieber, 1990; Lyons et al., 2000; Luepke and Lyons, 2001), early diagenetic barite (Rye et al., 1983; Strauss and Schieber, 1990), and carbonate associated sulfate (CAS; Ueda et al., 1987; Gellatly et al., 2000) in the ~ 1.4 Ga Belt Supergroup (Anderson and Davis, 1995; Aleinikoff et al., 1996) indicate that $\Delta^{34}\text{S}_{\text{max}}$ prior to the hypothesized 1.3 Ga oxygenation event fell within the range of $25\text{--}30\text{‰}$, consistent with predictions of Canfield and Teske (1996). Examination of $\Delta\delta\text{S}_{\text{max}}$ in the Society Cliffs Formation (Fig. 10), as well as from the ~ 1.2 Ga Grenville Supergroup (Whelan et al., 1990), suggests that $\Delta^{34}\text{S}_{\text{max}}$ in the late Mesoproterozoic, after the hypothesized rise in biospheric oxygen, also remained in the range of $25\text{--}30\text{‰}$, thereby supporting Canfield and Teske's assertion that oxygen-driven evolutionary innovations in the Neoproterozoic were required before biological sulfur fractionation could attain the present levels. An important consequence of this observation is that if the hypothetical $\Delta^{34}\text{S}_{\text{max}}$ of $25\text{--}30\text{‰}$ could be attained in the Mesoproterozoic, both before and after the hypothesized rise in biospheric oxygen at ~ 1.3 Ga, then *at no time in the Mesoproterozoic* were open marine, well-mixed waters sulfate-limited with respect to bacterial sulfate reduction.

5.2.3. Marine Mg/Ca ratios, carbonate saturation, and early diagenetic barite

If, as initial data suggest, open marine environments were not sulfate-limited with respect to bacterial sulfate reduction, it becomes difficult to interpret exactly what role ocean-atmosphere oxygenation may have played in the appearance and preservation of extensive bedded marine CaSO₄ evaporites in the Mesoproterozoic. As noted above, even in the later Mesoproterozoic, after the hypothesized oxygenation event, the size of the marine sulfate reservoir was not of sufficient magnitude to prevent marine systems from rapidly becoming isotopically limited with respect to bacterial sulfate reduction upon restriction from the open ocean. However, prior to ~1.3 Ga, the marine sulfate reservoir may have been small enough that bacterial sulfate reduction would effectively reduce the marine sulfate reservoir size before deposition of significant thicknesses of CaSO₄ evaporite minerals could occur. A limited oxygenation event at ~1.3 Ga may have sufficiently increased the marine sulfate reservoir, thereby facilitating widespread deposition of evaporite minerals prior to driving bacterial sulfate reduction to completion.

Evaporite deposition is not uncommon in successions older than 1.3 Ga, but rather is typically limited to small nodules and lenses of barite and carbonate pseudomorphs after gypsum or anhydrite (Rye et al., 1983; Walker et al., 1983; Muir et al., 1985; Strauss and Schieber, 1990; Deb et al., 1991). An alternate hypothesis for the Mesoproterozoic appearance of extensive bedded marine CaSO₄ evaporites, which challenges the primary role of Earth oxidation in sulfate deposition, was suggested by Grotzinger (1989). Based on sedimentologic examination of a large number of Proterozoic carbonate successions, Grotzinger (1989) suggested that Proterozoic marine waters may have had significantly greater carbonate saturation than that of Phanerozoic oceans, perhaps driven by elevated pCO₂, and therefore greater total DIC, in early Earth atmospheres (Walker, 1983; Kasting, 1987; Grotzinger and Kasting, 1993). Provided that marine systems remained buffered with respect to pH, perhaps via silicate weathering (Garrels, 1966; Spencer and Hardie,

1990), if DIC were elevated such that HCO₃⁻/Ca²⁺ ratios of Archean and Early Proterozoic marine waters approached or exceeded 2, enhanced precipitation of calcium carbonate may have impeded deposition of CaSO₄ minerals during seawater evaporation by effectively limiting the availability of Ca²⁺ for evaporite deposition (Grotzinger, 1989). This hypothesis is intriguing in that DIC-driven Ca²⁺-limitation would be expected to occur regardless of the size of the marine sulfate reservoir, thereby recognizing the possibility of a substantial marine sulfate reservoir in the post-2.0 Ga oceans, while accounting for the scarcity of pre-Mesoproterozoic CaSO₄ via changing marine carbonate saturation states. In fact, Grotzinger (1989) suggested that, prior to a decrease in DIC, such that HCO₃⁻/Ca²⁺ < 2, Proterozoic CaSO₄ deposition would have been restricted to marginal marine environments, where excess input of Ca²⁺ from weathering of continental basalts could have overcome effective marine Ca²⁺-limitation.

Resolution of these contrasting hypotheses regarding the driving force behind Proterozoic evaporite deposition is difficult. Although present data cannot conclusively determine the effects of the hypothesized Mesoproterozoic oxygenation event on sulfate reservoir size, elemental compositions of Society Cliffs evaporite minerals may provide a means of assessing the role of carbonate saturation on evaporite deposition. Marine brine compositions calculated from cation ratios within Society Cliffs evaporites suggest that Mesoproterozoic seawater had Ca²⁺, Sr²⁺, Na⁺, K⁺, and Ba²⁺ concentrations similar to the modern ocean, yet may have had substantially more Mg²⁺. Excess Mg²⁺, in the presence of elevated DIC, would have acted to further buffer marine systems from changes in pH by sustaining total marine alkalinity, thereby facilitating the expression of elevated atmospheric pCO₂ (Kasting, 1987) as enhanced carbonate saturation.

Elevated Mg²⁺ content of early oceans may be a natural consequence of higher heat flow in the early Earth. With greater temperatures of partial melting at mid-ocean ridges, oceanic crust would be expected to be increasingly Mg-rich and Ca-poor in composition (i.e. more komatiitic). Today, hy-

hydrothermal weathering of seafloor basalts are the dominant control of marine Mg^{2+} and Ca^{2+} concentrations (Spencer and Hardie, 1990). Typically, Ca^{2+} is released and Mg^{2+} is sequestered as clay minerals during hydrothermal alteration of young basalts (Spencer and Hardie, 1990), whereas both Ca^{2+} and Mg^{2+} are released from basalts during low-temperature weathering (Lasaga et al., 1985). The relative roles of these fluxes, however, are still in debate; for example, de Villiers and Nelson (1998) suggest, via measured Mg^{2+} anomalies at the East Pacific Rise, that low-temperature fluxes may exceed high-temperature fluxes by a factor of 10. Although metamorphic alteration of komatiites has been shown to result in significant Ca^{2+} depletion (T. Grove, pers. comm., 2000), weathering reactions in Mg-rich, Ca-poor basalts are poorly understood and may potentially have released significant excess Mg^{2+} into marine environments. Elevated Mg^{2+} concentrations in the Archean may have played an additional role in the inhibition of carbonate nucleation (Berner, 1975) and the formation of unusual abiotic carbonate textures (Sumner and Grotzinger, 1996a,b). In Proterozoic oceans, enhanced Mg^{2+} concentrations may have played a significant role in the facilitation of penecontemporaneous marine dolomitization (Folk and Land, 1975; Tucker, 1982; Kah, 2000).

In terms of the Proterozoic sulfate record, after the ~ 2.1 Ga rise in biospheric oxygen (Karhu and Holland, 1996), yet prior to the late Mesoproterozoic appearance of CaSO_4 evaporites, Mg^{2+} -driven carbonate hypersaturation would be expected to inhibit marine evaporite deposition by effectively limiting the oceans with respect to Ca^{2+} via enhanced carbonate precipitation (Grotzinger, 1989). Any deposition of CaSO_4 would occur in environments depleted in HCO_3^- as expected in most hybrid marine/non-marine fluids (Hardie and Eugster, 1970; Eugster and Hardie, 1978; Hardie, 1984), rather than under conditions of enhanced Ca^{2+} concentration (Grotzinger, 1989). Numerous examples of marginal marine sulfate evaporites are recorded in pre-1.3 Ga Mesoproterozoic and Paleoproterozoic successions (Cameron, 1983; Rye et al., 1983; Walker et al., 1983; Muir et al., 1985; Strauss and

Schieber, 1990; Deb et al., 1991), yet these occurrences, with the exception of anhydrite nodules in the Huronian Supergroup (Cameron, 1983), are comprised of barite pseudomorphs after CaSO_4 evaporites. We suggest that the preserved pre-1.3 Ga CaSO_4 evaporites originally precipitated from HCO_3^- -poor hybrid waters which, upon subsequent exposure to carbonate hypersaturated normal-to-hypersaline Mg^{2+} - and HCO_3^- -rich seawater during subsequent sea level fluctuations, would have become diagenetically unstable. Exposure of evaporites to normal salinity seawater would then have resulted in their rapid dissolution and formation of evaporite collapse breccias (cf. Pope and Grotzinger, 1997). Microscale dissolution-reprecipitation reactions during exposure of CaSO_4 evaporites to evaporative, high salinity marine waters would facilitate carbonate replacement of evaporite textures, or perhaps even barite precipitation. Although current marine surface waters are largely undersaturated with respect to barite (Monnin et al., 1999; Rushdi et al., 2000), evidence suggests that marine pore waters can rapidly become saturated with respect to barite and Sr-rich barite (Hanor, 1969; Rushdi et al., 2000) in anoxic and/or organic-rich environments (Falkner-Kennison et al., 1993), conditions that may have been met by hypersaline marine waters in the Proterozoic.

6. Conclusions

Isotopic and elemental analyses of evaporite minerals from the 1.2 Ga Society Cliffs Formation, Baffin Island, Canada, provide a means of assessing temporal trends in marine geochemistry within the context of hypotheses regarding Proterozoic ocean-atmosphere oxygenation, biogeochemical evolution, and changing marine carbonate saturation. Constraints from stratigraphy, isotopic and elemental compositions of associated carbonates, and cation ratios (Sr/Ca, Na/Ca, K/Ca) of evaporites all suggest a predominantly marine origin for Society Cliffs gypsum. This interpretation is further supported by Sr isotopic compositions that conservatively suggest, in all but a single stratigraphic interval, a less than 10%

non-marine contribution to evaporative waters. Given interpretation of a marine source for Society Cliffs gypsum, the preserved upsection, monotonic shift in $\delta^{34}\text{S}_{\text{sulfate}}$ from $\sim +22\%$ to $+32\%$ is interpreted as recording primary variation in marine sulfate compositions. The inferred rapidity of this 10‰ isotopic shift, which occurs over <300 m of stratigraphic section, suggests, however, that the Mesoproterozoic marine sulfate reservoir was significantly smaller than the present day sulfate reservoir; an interpretation consistent with significantly reduced pO_2 hypothesized for the late Neoproterozoic (Berkner and Marshall, 1965; Canfield, 1998). Furthermore, observed maximum isotopic fractionations of $\sim 25\%$ between syndepositional sulfate and sulfide species ($\Delta^{34}\text{S}_{\text{max}}$), support Canfield and Teske (1996) hypothesis that ocean-atmosphere oxygen levels did not reach levels sufficient for the evolution of oxic sulfur disproportionating bacteria until the Neoproterozoic. Furthermore, observed $\Delta^{34}\text{S}_{\text{max}}$ values near 25‰ are similar to the maximum fractionation of 25–30‰ for sulfur communities that lack oxic disproportionating bacteria but have excess SO_4^{2-} (Canfield and Thamdrup, 1994; Habicht and Canfield, 1996), indicating that the Mesoproterozoic sulfate, although smaller than at present, was not limiting with respect to microbial sulfate reduction.

The apparent contradiction between a potentially small marine sulfate reservoir and one that is not limiting with respect to bacterial sulfate reduction makes it difficult to determine how, if at all, a potential increase in pO_2 at ~ 1.3 Ga, inferred from the C-isotopic record (Kah et al., 1999), may relate to the appearance of bedded marine sulfates in the geological record at this time. Barite evaporites older than ~ 1.3 Ga, albeit volumetrically minor, are known from the geologic record, suggesting that an adequate sulfate reservoir existed prior to 1.3 Ga. Brine compositions calculated from cation ratios within Society Cliffs gypsum, however, suggest that Mesoproterozoic seawater may have had Mg^{2+} concentration significantly greater than modern seawater. Elevated Mg^{2+} contents would have sustained high marine alkalinity, which, in combi-

nation with potentially elevated pCO_2 (Grotzinger and Kasting, 1993) would have sustained high marine carbonate saturations. Mg-driven carbonate hypersaturation and enhanced carbonate precipitation may have effectively limited pre-1.3 Ga oceans with respect to Ca^{2+} during seawater evaporation, thereby prohibiting CaSO_4 deposition (Grotzinger, 1989). Yet in this scenario, Mg^{2+} and DIC act in concert to sustain elevated carbonate saturation. We suggest that probable ‘marine’ CaSO_4 evaporites deposited prior to ~ 1.3 Ga may have precipitated from hybrid marine/non-marine fluids depleted with respect to HCO_3^- . The appearance of CaSO_4 evaporites after 1.3 Ga, however, may record a critical transition of marine Ca^{2+} and Mg^{2+} concentrations with respect to DIC, and thereby represent a critical threshold in the marine carbonate saturation state of the Proterozoic oceans.

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