

Sedimentary cycling and environmental change in the Late Proterozoic: Evidence from stable and radiogenic isotopes

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(Received May 10, 1991; accepted in revised form December 11, 1991)

Abstract—We report C, Sr, and O isotopic as well as selected major and trace element data from Late Proterozoic (ca. 900–540 Ma) marine carbonates in three widely separated basins. The isotopic and elemental data are used to evaluate effects of post-depositional alteration of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$. Using our present best estimates for unaltered samples, we construct a new $\delta^{13}\text{C}$ -curve for 850–500 Ma marine carbonates using data in this paper and from literature sources. $\delta^{13}\text{C}$ values are high (+4 to +8‰) during most of the late Riphean (ca. 900–600 Ma) with brief negative excursions likely associated with glacial periods. Similarly, in the Vendian $\delta^{13}\text{C}$ falls sharply (from late Riphean highs) to $< -3\%$ around the Varanger glaciation (ca. 600 Ma), and then returns to high values (+4 to +2‰) remaining until the Precambrian-Cambrian boundary where the curve drops to a value of about -1% in Lower Cambrian carbonates. Coupling of the Sr and C isotopic data is used to develop a simple model for evaluating organic carbon (C_{org}) burial in Late Proterozoic oceans. These calculations indicate that C_{org} burial rates were lower than present-day values during much of the late Riphean, at the same time that erosion rates were low. Excess O_2 produced by the burial of C_{org} was likely balanced by oxidation of reduced hydrothermal fluids and weathering reactions. Near the time of the Varanger glaciation, C_{org} burial rates dropped but quickly recovered and reached a maximum (a factor of 2–4 greater than present day) in Vendian sediments. High C_{org} burial rates were probably driven by high sedimentation rates, and possibly high productivity. The high C_{org} burial rate likely gave rise to a large flux of O_2 ; high values of $\delta^{34}\text{S}$ in Late Proterozoic marine sulfates suggest that this O_2 flux was not balanced by increased sulfate formation. Further, the Sr-isotopic record indicates that excess O_2 was not balanced by oxidation of submarine hydrothermal fluids. Increased oxidative weathering was probably an important sink for O_2 ; nonetheless, we conclude that a significant and rapid increase in atmospheric O_2 occurred in the Vendian. These results have important implications for environmental changes during the first appearance of an Ediacaran meta-zoan fauna.

INTRODUCTION

INCREASING GEOLOGICAL, geochemical, and paleontological evidence points to the Late Proterozoic (900–540 Ma) as a particularly interesting period in Earth history. The geological record shows evidence for the existence and breakup of an early supercontinent during the late Riphean (BOND et al., 1984; LAMBERT and DONNELLY, 1992). After a depositional hiatus of nearly 1 Ga. (cf. JAMES, 1983), there is sudden reappearance of sedimentary iron formations on five continents. Significantly, these iron formations are typically interbedded with glacial strata (YOUNG, 1976; YEO, 1981; KAUFMAN et al., 1991) apparently older than 650 Ma. In contrast, glacial strata deposited during the widespread Varanger episode (ca. 590–600 Ma) have no associated iron formations. In the Vendian, the widespread Pan-African orogenic event affected much of present-day Africa, Europe, and Asia (cf. BOND et al., 1984; PORADA, 1989). The Vendian-to-Cambrian transition was also a time of massive phosphorite deposition (COOK and MCELHINNEY, 1979).

Micropaleontologic evidence suggests that the Vendian period of massive phosphogenesis coincided with the extinction of many taxa of marine plankton (VIDAL and KNOLL 1982), and the evolution of the first distinct nonskeletal Edi-

acaran animals (GLAESSNER, 1984). Microfossils, particularly acritarchs of probable phytoplanktonic origin, appear to diversify rapidly in Late Proterozoic oceans (BUTTERFIELD et al., 1988), and several biostratigraphic zones have been identified and appear to be useful in the correlation of widely separated Late Proterozoic basins.

Marine carbonates deposited in the late Riphean and Vendian show strong and rapid variations in the isotopic composition of C and Sr (e.g., KNOLL et al., 1986; DERRY et al., 1989; KAUFMAN et al., 1991; ASMEROM et al., 1991). These fluctuations suggest important variations in Late Proterozoic exogenic cycle and could have significant implications for the evolution of Late Proterozoic environments.

Detailed understanding of this environmental change requires the ability to recover primary isotopic signatures from Late Proterozoic marine carbonates. In this paper we evaluate post-depositional diagenetic effects on primary isotopic compositions of a variety of limestones and dolomites from Vendian and late Riphean sedimentary successions worldwide. Provided with geochemical parameters to evaluate variably altered sediments, we then present new and compiled data on the C and Sr isotopic evolution of Late Proterozoic seawater. From detailed knowledge of the timing and variation of these secular changes we attempt a simple model to explain the geochemical relationships. Further, we explore the implications of these relationships for changes in global geochemical cycles, particularly the burial of organic carbon

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(C_{org}), and thus, indirectly, the evolution of atmospheric O_2 during the Late Proterozoic.

SAMPLES AND AGES

Samples from three Late Proterozoic basins in Namibia, Svalbard and East Greenland, and Australia were selected for detailed geochemical analysis. The basins and samples are only briefly described below; more complete descriptions are available in the cited references.

Ages of stratigraphic groups were estimated from the best available geochronologic information presently available; ages of individual samples within these groups were calculated using an empirical basin subsidence model (cf. DERRY et al., 1989). We used an age of ca. 540 Ma for the Precambrian/Cambrian boundary (ODIN et al., 1985; CONWAY MORRIS, 1989) and ca. 590–610 for the Varanger glaciation (KROGH et al., 1988; KAYE and ZARTMAN, 1985; see compilation of all ages in CONWAY MORRIS, 1989).

Nama and Witvlei Groups, Namibia

The Vendian to Early Cambrian Nama and Witvlei groups consist of thick sequences of limestones, dolomites, and terrigenous sediments deposited during an extensive marine transgression over the Kalahari Craton in Namibia (KAUFMAN et al., 1991). Carbonates of the Nama Group used in this study are typically composed of laminated or massive calcite microspar with minor amounts of sparry calcite. In contrast, Witvlei Group carbonates are composed predominantly of dolomicrospar. High Sr contents in many of the Nama Group limestones suggest an original aragonitic mineralogy for these carbonates (GRANT et al., 1991).

The Nama Group with its distinctive Ediacaran animals and the underlying Witvlei Group must be latest Proterozoic in age. All of the Nama Group and at least the upper half of the Witvlei Group sit above glacial rocks of Varanger age. Carbonates from these groups are constrained to be older than the Precambrian-Cambrian boundary now at 540 Ma and younger than 600 Ma. Carbon isotope chemostratigraphic correlation with other boundary sections suggests that the Namibian rocks comprise the most complete coverage through this time period (see KAUFMAN et al., 1991).

Oslobreen, Polarisbreen, Akademikerbreen, and Veteranen Groups, Svalbard and East Greenland

The late Riphean to Early Cambrian sedimentary successions of Svalbard and East Greenland consist of approximately 6000 m of carbonates, shales, siliciclastics, and minor diamictites. The Akademikerbreen and Polarisbreen groups of Svalbard archipelago and East Greenland are now separate parts of a once contiguous basin. These sections are well correlated by litho-, bio-, and chemo-stratigraphic techniques (FAIRCHILD and HAMBREY, 1984; HARLAND, 1983; KNOLL and SWETT, 1990). Samples used in this study include micritic, oolitic, and stromatolitic limestones and dolostones.

Samples from the Oslobreen Group are Lower Cambrian in age. Unconformably beneath this group is the Polarisbreen group, which contains Varangian sediments (590–610 Ma). We estimate this group to span ca. 570 to 630 Ma. We retain our previous estimate of 700–800 Ma ages for the Akademikerbreen Group (DERRY et al., 1989). The bottom of this group (Svanbergfjellet and Grusdievbreen formations) appears to be correlative with the upper Shaler Group which is fairly well dated at ca. 766 ± 24 Ma (see discussion in ASMEROM et al., 1991). Only uppermost Veteranen samples are used in the present compilation and are given dates between 800–810 Ma.

Bitter Springs Formation, Central Australia

The Bitter Springs Formation in the Amadeus Basin of central Australia overlies the Heavitree Quartzites and sits unconformably below diamictites of the Areyonga and Boord formations. Samples in this study are from the shallow marine to continental Loves Creek Member which contains limestones and dolomites partially interbedded with siliciclastics (SOUTHGATE, 1986, 1989). The samples are from marine, evaporitic, and lacustrine facies, including upward shallowing stromatolite cycles (Southgate, pers. comm.).

The Bitter Springs Formation is presently of unknown age. HAYES et al. (1992) mention $^{87}\text{Sr}/^{86}\text{Sr}$ values from evaporites in the range 0.7057–0.7064. These values are comparable to the ca. 830 Ma rocks of the Shaler Group (ASMEROM et al., 1991) and suggest that this age may be appropriate for Bitter Springs. However, DESMARAIS and SOUTHGATE (1990) report $\delta^{13}\text{C}$ values from marine carbonates about -1 and note that these values are typical of mid-Riphean carbonates. Alternatively, such low values could also be associated with one of the late Riphean negative excursions related to glacial events (cf. KAUFMAN et al., 1991). A negative excursion occurs at about 850 Ma in the C isotope record, and we tentatively propose an age of 825–850 Ma for the Bitter Springs Formation.

ANALYTICAL PROCEDURES

Carbonate samples were broken into chips which were subsequently picked for clean fragments. These chips were crushed in a stainless steel mortar. Two splits of each powder were weighed (typically <100 mg) and leached in ultraclean 0.5 M acetic acid. Our experience shows that this method is preferable to using even fairly dilute (ca. 1 N) HCl. HCl is more aggressive toward clastic components in the carbonates, such as clay minerals, and we have observed a pattern of higher $^{87}\text{Sr}/^{86}\text{Sr}$, Rb/Sr, and Th/U ratios in splits treated with HCl relative to those treated with acetic acid. The solutions were centrifuged and decanted, and residues were dried and weighed to determine percent dissolution. One split was evaporated to dryness and redissolved in 2% HNO_3 . Major and trace element analyses were performed on a VG PQ2 plasma source mass spectrometer using gravimetrically determined standards to develop calibration curves and a ^{115}In spike for normalization. The other split was dried and redissolved in HCl and a small ($\sim 1\%$) aliquot was taken and spiked with isotopic tracers for Rb and Sr. Concentrations of these elements were determined by isotope dilution on a VG-54 thermal ionization mass spectrometer. Strontium in the remaining split was isolated by standard ion exchange techniques and isotopic compositions determined in a Finnigan-MAT 262 thermal ionization instrument with static multi-collection. Interference from ^{87}Rb was controlled by measuring ^{85}Rb with an SEM in ion counting mode. NBS987 standards run with each sample magazine yield an average value during the course of this work of 0.710241 ± 8 (uncertainty given as two sigma of the mean). Pacific seawater was measured at 0.709174 ± 5 . A third split of finely powdered sample was loaded into the auto-sampler magazine of a VG Prism isotope ratio instrument. The samples were reacted on line with H_3PO_4 ($\rho > 1.89$ g/mL) and exsolved CO_2 was measured for carbon and oxygen isotopic compositions. Reaction times of 10 min were used to obtain quantitative yields in the phosphorolysis of dolomites. Fractionation factors employed for calculation of ^{18}O abundances of calcites and dolomites based on analysis of CO_2 prepared at 90°C were 1.00798 and 1.00895, respectively.

RESULTS

Diagenetic Effects and Primary Isotopic Signatures

The isotopic compositions of Sr and C in marine carbonates are susceptible to alteration. The processes of alteration may include early diagenetic transformations, late diagenetic fluid-rock reaction, hydrothermal activity, and metamorphism, among others. Since it is not possible to evaluate each of these processes independently, we have attempted to develop empirical indicators for the effects of post-depositional alteration on the Sr and C isotopic systematics of marine carbonates. Our objective is to determine which samples are most likely to represent a record of the isotopic composition of coeval seawater, and so construct curves for the evolution of Sr and C isotopes in seawater with some confidence. We expect that the criteria for evaluating Sr, a trace element in marine carbonates, may not be the same as for C, a major component. To this end we have measured the abundances

of selected major and minor elements, and the isotopic compositions of C, Sr, and O in samples from several Late Proterozoic sequences. We use the combined data set to evaluate the C and Sr isotopic data for effects of alteration.

Isotopic and chemical data for each section are reported in Table 1. In Fig. 1 we present some examples of the types of correlations evident in the data. High $^{87}\text{Sr}/^{86}\text{Sr}$ values from all the sections are associated with high Mn/Sr values. In

Table 1. Analytical Data and Initial Values of Carbonate Samples.

Sample	Rb*	Sr*	$\left[\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right]$	$\left[\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right]$ **	$\left[\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right]_I$	$\delta^{13}\text{C}\dagger$	$\delta^{18}\text{O}\dagger$	Mn/Sr	Ca/Sr	Mg/Ca	Age(Ma)
A. Bitter Springs											
<i>I. Saline Pond</i>											
97.12	0.070	51.9	0.0036	0.70950±2	0.70946±2	+3.48	-5.85	16.8	2485	0.484	850
107.00	0.640	76.8	0.0240	0.70799±2	0.70770±2	+3.44	-7.77	2.90	2852	0.007	850
<i>II. Lake</i>											
133.20	0.120	78.5	0.0043	0.70892±1	0.70887±1	+4.66	-5.73	6.19	1868	0.224	850
141.48	0.280	192	0.0043	0.70881±1	0.70876±1	+4.12	-10.69	1.91	1781	0.006	850
<i>III. Marine</i>											
228.80	0.060	114	0.0014	0.70740±2	0.70738±2	-1.63	-8.55	0.862	2151	0.006	850
229.18	0.200	128	0.0045	0.70815±1	0.70810±1	-1.10	-10.02	1.03	2399	0.006	850
279.64	0.080	32.4	0.0072	0.70857±1	0.70848±1	-2.68	-8.33	11.1	4564	0.547	850
286.87	0.170	22.2	0.0216	0.70950±1	0.70924±1	-2.09	-8.40	9.96	4354	0.516	850
288.23	0.050	25.8	0.0056	0.71114±1	0.71107±1	-2.36	-11.44	14.6	5727	0.456	850
305.67	0.040	20.1	0.0059	0.70927±1	0.70920±1	-2.86	-8.77	8.03	4052	0.518	850
315.90	0.080	20.1	0.0120	0.70889±1	0.70874±1	-2.85	-8.36	12.5	6087	0.534	850
316.25	0.080	19.9	0.0113	0.70944±1	0.70930±1	-2.84	-7.99	11.9	6387	0.554	850
B. Svalbard and East Greenland											
<i>I. Polarbreen group</i>											
P7380SB	0.772	637	0.0035	0.70704±2	0.70701±2	+4.04	-2.01	1.93	2350	0.552	610
Gr-20EG	0.276	705	0.0013	0.70728±5	0.70727±5	-4.24	-6.75	3.94	811	0.087	613
M-38SB	0.217	2369	0.0003	0.70679±7	0.70679±7	+6.15	-4.17	0.180	778	0.011	614
M-37SB	0.441	1768	0.0007	0.70693±7	0.70692±7	+1.16	-5.89	0.785	776	0.009	615
<i>II. Akademikerbreen group</i>											
P-6010SB	0.232	281	0.0024	0.70684±4	0.70682±4	+6.62	-6.70	0.173	595	0.009	705
P-115SB	0.680	1830	0.0011	0.70663±4	0.70662±4	+6.79	-4.95	0.184	585	0.008	715
P-114SB	0.166	246	0.0020	0.70703±5	0.70701±5	+8.54	-2.38	0.693	3101	0.568	718
P-109SB	0.377	201	0.0054	0.70718±2	0.70712±2	+6.21	-5.15	0.530	2838	0.553	729
K-1325NL	0.069	2350	0.0001	0.70710±7	0.70710±7	+8.20	-	0.019	160	0.030	741
P-42SB	0.184	1725	0.0003	0.70686±3	0.70686±3	+8.37	-4.95	0.016	198	0.009	744
P-39SB	0.183	237	0.0022	0.70716±4	0.70714±4	+4.87	-5.02	0.520	990	0.031	747
Gr-2580EG	0.119	1088	0.0003	0.70720±3	0.70720±3	+7.20	-6.80	0.223	350	0.007	749
P-9SB	0.330	1831	0.0005	0.70715±2	0.70715±2	+5.88	-5.27	0.398	638	0.500	760
P-4085SB	0.130	225	0.0017	0.70704±3	0.70702±3	+6.60	-1.88	0.759	1432	0.587	763
G-41SB	1.485	1040	0.0041	0.70696±5	0.70692±5	+5.49	-5.31	0.992	1083	0.014	770
K-1275NL	0.340	540	0.0018	0.70757±2	0.70755±2	+4.20	-2.09	0.178	454	0.590	774
G-19SB	0.157	2436	0.0002	0.70621±5	0.70620±5	+7.16	-4.79	0.003	217	0.005	778
GR-10SB	0.050	401	0.0004	0.70940±7	0.70940±7	-1.40	-7.78	0.246	788	0.006	779
G-13SB	0.437	670	0.0019	0.70740±4	0.70738±4	-1.50	-4.88	0.641	1142	0.423	781
K-1260NL	0.665	762	0.0025	0.70733±4	0.70731±4	-1.20	-5.68	0.343	1785	0.166	782
P-2355SB	0.116	2474	0.0001	0.70667±5	0.70667±5	+0.86	-9.35	0.004	154	0.003	784
F-32SB	0.058	1685	0.0001	0.70651±4	0.70651±4	-0.06	-7.33	0.006	249	0.005	786
F-27SB	0.459	370	0.0037	0.70650±3	0.70646±3	+1.43	-9.04	0.103	1177	0.008	789
F-18SB	0.381	842	0.0013	0.70678±6	0.70677±6	+5.87	-6.57	0.058	566	0.016	792
P-57SB	0.869	1204	0.0021	0.70675±2	0.70673±2	+3.34	-7.73	1.34	671	0.009	794
<i>III. Veteranen group</i>											
F-10SB	0.310	622	0.0015	0.70824±3	0.70822±3	+4.19	-14.87	5.71	1155	0.009	807
F-12SB	0.226	228	0.0029	0.71197±4	0.71194±4	+2.19	-14.90	15.9	1757	0.007	810
C. Nama											
SN75	0.270	349	0.0022	0.70940±1	0.70938±1	+1.80	-9.36	0.243	281	0.240	550-575
SS17	0.096	1591	0.0002	0.70851±1	0.70851±1	+1.73	-8.06	0.045	83.7	0.002	550-575
SH54	0.115	708	0.0005	0.70868±2	0.70868±2	+1.46	-8.65	0.033	161	0.003	550-575
SH49	0.055	1979	0.0001	0.70849±1	0.70849±1	+1.57	-7.51	0.034	156	0.005	550-575
KMO92	0.847	453	0.0115	0.70977±1	0.70967±1	+4.79	-13.05	0.792	643	0.005	550-575
KO137	0.053	3596	0.0000	0.70840±1	0.70840±1	-	-	-	-	-	550-575
KO140	0.127	471	0.0008	0.70903±1	0.70902±1	+1.91	-8.76	0.424	551	0.012	550-575
KMO5	0.075	245	0.0009	0.71052±1	0.71052±1	-1.24	-13.25	0.541	946	0.004	550-575
KM3	0.356	64.7	0.0153	0.71025±1	0.71013±1	-5.18	-3.10	15.7	1525	0.539	550-575
KM111	0.203	340	0.0011	0.71141±1	0.71140±1	-1.96	-12.26	5.65	786	0.009	550-575
D. Witvlei											
203	0.139	55.5	0.0070	0.71331±2	0.71326±2	-2.92	-5.34	8.24	2070	0.565	575-600
393	0.116	57.6	0.0056	0.71560±1	0.71555±1	-4.60	-3.86	4.83	2334	0.235	575-600
159	0.037	79.3	0.0013	-	-	+1.73	-3.71	11.4	1188	0.575	575-600
188	0.034	31.4	0.0030	0.71860±1	0.71857±1	-3.74	-6.43	6.81	1912	0.564	575-600

* All concentrations (ppm) are calculated for the dissolved fraction.

** $^{87}\text{Sr}/^{86}\text{Sr}$ measured using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ to correct for fractionation in the mass spectrometer.

$^{87}\text{Sr}/^{86}\text{Sr}$ value of modern seawater measured in this lab = 0.709174 ± 5 .

† $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are given relative to the PDB standard and have typical uncertainties of ± 0.1 and ± 0.2 respectively.

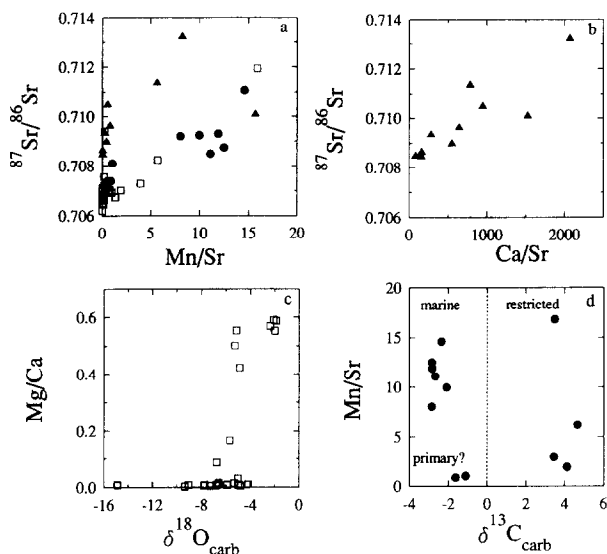


FIG. 1. Radiogenic, stable isotope, and elemental data on Late Proterozoic marine carbonates from the Bitter Springs Formation in Australia (filled circles), the Akademikerbreen and Polarisbreen groups in Svalbard and equivalents in East Greenland (open squares), and the Nama and Witvlei groups in Namibia (filled triangles). Figure includes (a) all samples, (b) Nama and Witvlei groups, (c) Akademikerbreen Group, and (d) Bitter Springs Formation.

addition, samples from the Nama and Witvlei groups have a significant correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Sr. In all successions, $^{87}\text{Sr}/^{86}\text{Sr}$ does not vary strongly with $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$, although very negative $\delta^{18}\text{O}$ values (< -9) are nearly always associated with anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Data from the Bitter Springs Formation show very low Sr concentrations ([Sr]), and a significant dependence of $^{87}\text{Sr}/^{86}\text{Sr}$ on [Sr]. As with the Namibian samples, this dependence suggests that the Sr can be described by two components, a mixture between a high concentration, unradiogenic source, and a low concentration, radiogenic source. The Svalbard and East Greenland samples were pre-screened using Rb and Sr concentrations, and most of those that had high $^{87}\text{Rb}/^{86}\text{Sr}$ or very low [Sr] were not analyzed further (DERRY et al., 1989). Consequently, the data set from this area is biased toward unaltered samples, and similar alteration trends are not as apparent.

In each example the data indicate variable degrees of fluid-rock alteration of the primary carbonates. The high concentrations of Sr in some of the Spitsbergen and Namibia samples suggest that the original mineralogy of these samples contained aragonite. Recrystallization during the aragonite-calcite transition can cause loss of Sr (KATZ et al., 1972). As indicated above, the variations of $^{87}\text{Sr}/^{86}\text{Sr}$ with [Sr] and Rb/Sr in the Nama and Bitter Springs sequences indicate that the rock has exchanged with a low [Sr], high $^{87}\text{Sr}/^{86}\text{Sr}$ fluid. The very low $\delta^{18}\text{O}$ values associated with anomalous $^{87}\text{Sr}/^{86}\text{Sr}$ also reflect fluid alteration (cf. ZEMPOLICH et al., 1988). The Mn-Sr systematics support this view. Mn/Sr ratios in modern seawater are very low, ca. 10^{-5} (cf. HOLLAND, 1978), whereas data from formation waters and geothermal wells show variable but much higher ratios, (Mn/Sr = 0.02 to 3; e.g., KHARAKA et al., 1977). Partition coefficients for Sr and Mn (K_{Sr}

and K_{Mn}) between calcite and aqueous solutions give a ratio $K_{\text{Mn}}/K_{\text{Sr}} = 2 \cdot 10^3$ (LORENS, 1981). Thus, Mn/Sr ratios should be a sensitive indicator of alteration in marine carbonates (cf. VEIZER, 1983; POPP et al., 1986). The trends apparent in the trace element, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ data for each set of samples are consistent with the reaction of Sr-rich primary carbonates, with fluids that have low Sr contents, and high $^{87}\text{Sr}/^{86}\text{Sr}$, Mn/Sr, and Rb/Sr values. Because of the low C contents of most diagenetic fluids relative to the high carbon content of carbonate rocks, such reaction will not necessarily be reflected in $\delta^{13}\text{C}$ -values.

Many of the Witvlei and Bitter Springs samples are dolomitic, and have very low [Sr] which correlates negatively with $^{87}\text{Sr}/^{86}\text{Sr}$. Strontium loss is significant during dolomitization because of the smaller K_d for Sr between dolomite and water than calcite and water (e.g., KATZ and MATTHEWS, 1977; VAHRENKAMP and SWART, 1990). The Witvlei samples have variable $\delta^{18}\text{O}$ values, high Mn/Sr ratios, and very high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The Sr isotope compositions of these samples appear to have been substantially altered during dolomitization and do not provide a good constraint on seawater compositions. There is also a correlation between Mn/Sr and $\delta^{13}\text{C}$, which suggests that the primary values of $\delta^{13}\text{C}$ in the Witvlei Group may have been quite low (ca. -3‰). Bitter Springs samples show similar patterns. While oxygen compositions are variable, all have high Mn/Sr ratios. Two limestones have significantly higher [Sr], and lower Mn/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ values than dolomites from the same environment. The relatively low values of $^{87}\text{Sr}/^{86}\text{Sr}$ obtained from these two samples indicate that coeval seawater was no higher than 0.7074, but this is only a likely upper limit. VEIZER et al. (1983) reported a value of 0.7068 for a Bitter Springs carbonate, while HAYES et al. (1992) report values from sulfates of 0.70568 to 0.70636. These low values may be better estimates of coeval seawater. Mg/Ca, Mn/Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ all show some correlation with $\delta^{13}\text{C}$ values in the marine samples. These trends suggest that the primary $\delta^{13}\text{C}$ value of the marine samples may have been close to -1.5‰ (Fig. 1d), and that the $\delta^{13}\text{C}$ of the dolomitized marine samples have been shifted about -1.5‰ . Four of the Bitter Springs samples are probably from non-marine environments (Southgate, pers. comm.). In both cases the limestones again have higher [Sr] and lower $^{87}\text{Sr}/^{86}\text{Sr}$ than the dolostones. In these samples the high $\delta^{13}\text{C}$ values are consistent with a restricted environment. Our inferences from the $\delta^{13}\text{C}$ patterns in the Bitter Springs samples are consistent with the independent assessment of DESMARAIS and SOUTHGATE (1990). The data from the Bitter Springs carbonates suggest that all of the samples we measured show signs of significant alteration.

Three limestone samples from the upper Nama Group are characterized by Mn/Sr < 0.1 , $\delta^{18}\text{O} \approx -8\text{‰}$, and $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7085$. All other Nama samples have either high Mn/Sr, anomalous $\delta^{18}\text{O}$, or both. These samples represent our best estimate of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater during this time. The $\delta^{13}\text{C}$ systematics of these samples suggest that the primary $\delta^{13}\text{C}$ was 1.5 to 2.0‰. Most of the lower Nama and Witvlei samples appear to have variably altered Sr isotopic compositions. The least-altered samples again suggest a primary $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7084, with a range of primary $\delta^{13}\text{C}$ values. The C-isotopic values for the Nama and Witvlei group samples estimated

from the combined Mn-Sr- $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ systematics are in agreement with the values obtained by KAUFMAN et al. (1991) from a detailed study of carbonate cements and coexisting organic matter.

Primary $^{87}\text{Sr}/^{86}\text{Sr}$ values from the Akademikerbreen Group appear to be consistently close to 0.707 (cf. DERRY et al., 1989). All of the anomalous samples have high Mn/Sr or very low $\delta^{18}\text{O}$ ($< -9\%$) values (Fig. 1). Limestone samples with Mn/Sr < 1 define trends in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ values which show good correlation, suggesting that these variations are primary (Fig. 2). Unlike our other examples, a number of dolostones appear to have $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ values very consistent with those in limestones. However, some of the dolostones have slightly higher $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values than the limestones, but the $\delta^{13}\text{C}$ values are indistinguishable (Figs. 1c, 2a, c). The new data reinforce the notion that the carbonates of the Akademikerbreen Group are particularly well preserved (KNOLL et al., 1986; KNOLL and SWETT, 1990). $\delta^{18}\text{O}$ in these least-altered samples is typically ca. -6% , but drops to ca. -8% at the same time as a strong drop in $\delta^{13}\text{C}$ values (Fig. 2). This $\delta^{13}\text{C}$ excursion appears to coincide with the Sturtian glacial epoch (KNOLL et al., 1986). Relations for the "least-altered" Akademikerbreen Group samples appear to be crudely generalizable to the samples from other sequences: $\delta^{18}\text{O}$ between -4 and -9% ; Mn/Sr < 1 ; Ca/Sr < 1000 . However, no one indicator used alone is capable of detecting alteration in all cases. The integrated use of several tracers of alteration processes is necessary to effectively screen the sample population.

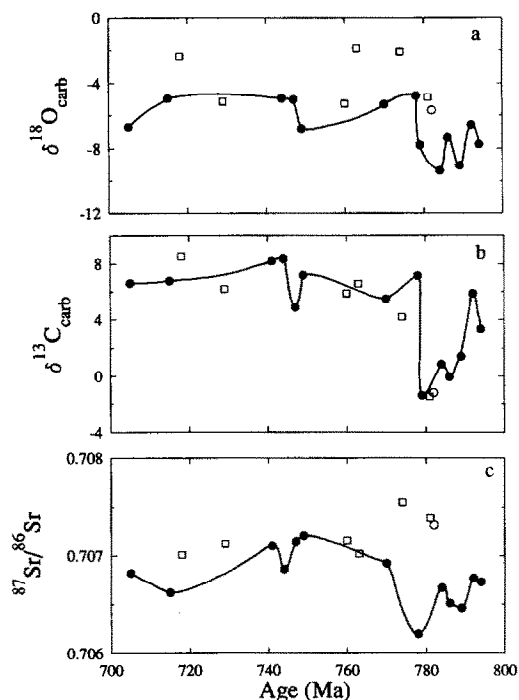


FIG. 2. Secular variations in (a) $\delta^{18}\text{O}$, (b) $\delta^{13}\text{C}$, and (c) $^{87}\text{Sr}/^{86}\text{Sr}$ of marine carbonates from the Akademikerbreen Group in Svalbard and equivalents in East Greenland. Strontium isotope data from DERRY et al. (1989). Filled circles represent least-altered limestones with Mn/Sr < 2 and $\delta^{18}\text{O} > -10$. Open symbols represent altered limestones (circles) with Mn/Sr > 2 or dolomites (squares).

Detailed studies of $\delta^{13}\text{C}$ in whole-rock vs. micritic cements have shown that in a number of Late Proterozoic sequences the two are comparable (FAIRCHILD and SPIRO, 1987; AHARON et al., 1987; KAUFMAN et al., 1991). These results indicate that whole-rock C isotope compositions have not been significantly altered by diagenetic fluids. It has been suggested that the retention of primary $\delta^{13}\text{C}$ values in Late Proterozoic carbonates is favored by low initial porosity and very early lithification (BURDETT et al., 1990; KNOLL and SWETT, 1990; KAUFMAN et al., 1991). In Late Proterozoic marine carbonates from the Bitter Springs, Witvlei, and Mauritania (FAIRCHILD et al., 1990), alteration of $\delta^{13}\text{C}$ values is associated with large increases in [Mn]. The evidence suggests that alteration sufficiently severe to strongly affect C isotope values in the Late Proterozoic should be readily recognizable with trace element and other isotopic data. The majority of samples that we studied do not show evidence for such extensive alteration, and these samples yield a good estimate of primary $\delta^{13}\text{C}$ values.

C-Isotopic Variations in 850–500 Ma Seawater

Secular variations in $\delta^{13}\text{C}$ of marine carbonates from 850 to 500 Ma are plotted on Fig. 3. Data are compiled from published analyses of Late Proterozoic carbonates by KNOLL et al. (1986), FAIRCHILD and SPIRO (1987), KAUFMAN et al. (1991), ASMEROM et al. (1991), and new $\delta^{13}\text{C}$ determinations on the Akademikerbreen Group. The present compilation includes only limestones and dolomites containing $>50\%$ carbonate; no organic $\delta^{13}\text{C}$ data are presented. The apparent gap in the data between about 700 and 650 Ma is caused by an unconformity at the top of the Akademikerbreen Group of Svalbard (KNOLL and SWETT, 1990). Because a reliable estimate of the age of the sediments at the top of this group is unavailable, we are uncertain of the duration of this hiatus (cf. discussion in DERRY et al., 1989).

KNOLL et al. (1986) have shown that most Late Proterozoic marine carbonates are strongly enriched in ^{13}C . In their $\delta^{13}\text{C}$ curve both carbonate and organic C from Svalbard and East Greenland are used to constrain secular variations in the $\delta^{13}\text{C}$ signature of Late Proterozoic seawater. The C-isotopic composition of organic C covaries with that of carbonate C in these unmetamorphosed sediments, suggesting that isotopic variations are primary in nature. However, the estimated uncertainty in the average fractionation between $\delta^{13}\text{C}$ of carbonate C (δ_{carb}) and of organic C (δ_{org}) expressed as

$$\Delta = \delta_{\text{carb}} - \delta_{\text{org}} = 28.5 \pm 2.0 \quad (1)$$

is relatively large. The scatter in the Δ values is probably caused by diagenetic and thermal alteration of organic matter, resulting in variability in the $\delta^{13}\text{C}$ of organic carbon. In more altered sediments the effect on organic carbon $\delta^{13}\text{C}$ values is larger (cf. KAUFMAN et al., 1991), and we therefore base the curve on secular variation of marine carbonate $\delta^{13}\text{C}$ values alone.

The new data and compilation confirm the high $\delta^{13}\text{C}$ values of Late Riphean and Vendian carbonates, and better constrain the strong variations during this time. The widespread occurrence of isotopically heavy carbonates ($\delta^{13}\text{C} \geq +5\%$) implies enhanced burial of organic carbon on a global basis

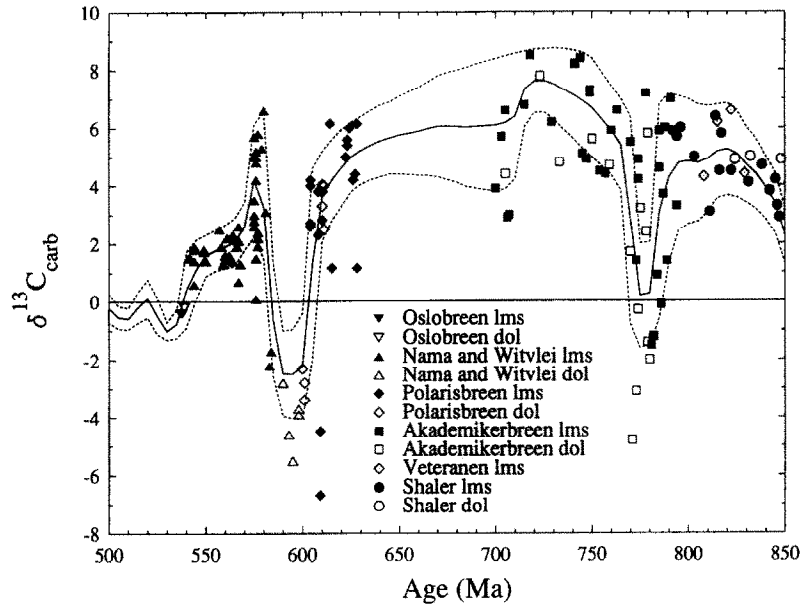


FIG. 3. Secular variations in $\delta^{13}\text{C}$ of Late Proterozoic marine carbonates from the Nama and Witvlei groups in Namibia (KAUFMAN et al., 1991), the Osloebreen, Polarisbreen, Akademikerbreen, and Veteranen groups in Svalbard and equivalents in East Greenland (KNOLL et al., 1986, and this study), and the Shaler Group in Victoria Island, Arctic Canada (ASMEROM et al., 1991). Ages of stratigraphic groups were estimated from the best available geochronologic information presently available; ages of individual samples within these groups were calculated using an empirical basin subsidence model. Negative excursions in the $\delta^{13}\text{C}$ curve coincide with the Varangian (ca. 600 Ma) and Sturtian (ca. 780 Ma) glacial episodes.

(e.g., KNOLL et al., 1986). Intervals of negative $\delta^{13}\text{C}$ indicate brief periods of more limited organic C burial, which correlate with glacial epochs (KNOLL et al., 1986; KAUFMAN et al., 1991). The highly negative values ($\delta^{13}\text{C} < -5\text{‰}$) observed in a few samples cannot record open marine conditions, as this would violate the isotopic mass balance of the exogenic C system. Two explanations may apply: (1) these carbonates formed in a restricted environment that was not open to carbon exchange with the whole ocean or (2) they contain a large percentage of carbonate formed during diagenetic oxidation of organic carbon. In contrast, low values ($\delta^{13}\text{C} = -2$ to -4‰) are found in samples of Varangian age from two separate localities and appear to be primary. After the Varanger ice age (ca. 590–610 Ma), $\delta^{13}\text{C}$ values of marine carbonates increased rapidly to near preglacial values, then decreased to values around $+2\text{‰}$ which remained until the Precambrian-Cambrian boundary. Cambrian values are consistently negative averaging around -1‰ . $\delta^{13}\text{C}$ variations have been reported from a number of other Precambrian-Cambrian boundary sections (e.g., MAGARITZ et al., 1986; LAMBERT et al., 1987; AHARON et al., 1987), and these are consistent with those observed in Namibia (KAUFMAN et al., 1991).

We interpret the isotopic variations in the carbonate reservoir as reflecting changes in the mass balance of sedimentary C between the oxidized and reduced reservoirs (e.g., BROECKER, 1970). The carbon cycle, to a first approximation, can be considered a balance between the C in the carbonate rock reservoir and the organic reservoir. The mass fraction of C in the organic C reservoir is

$$X_{\text{org}} = M_{\text{org}} / (M_{\text{org}} + M_{\text{carb}}) = M_{\text{org}} / M_{\text{tc}} \quad (2)$$

where M_{carb} , M_{org} , and M_{tc} are the masses of carbonate, organic, and total exogenic carbon (tc), respectively. The isotopic mass balance between the organic and carbonate C reservoirs is

$$\delta_{\text{tc}} = (1 - X_{\text{org}}) \langle \delta_{\text{carb}} \rangle + X_{\text{org}} \langle \delta_{\text{org}} \rangle \quad (3)$$

where $\langle \delta_{\text{carb}} \rangle$ is the average $\delta^{13}\text{C}$ -value of the sedimentary carbonate reservoir and $\langle \delta_{\text{org}} \rangle$ is the average $\delta^{13}\text{C}$ -value of the sedimentary organic C reservoir. The values of the reservoirs are related by the total exogenic carbon $\delta^{13}\text{C}$ value (assumed equal to the bulk earth value) of $\delta_{\text{tc}} = -5.5\text{‰}$ (DESMARIS and MOORE, 1984; MATTEY et al., 1984). We assume that Δ values are essentially constant through the Late Proterozoic and introducing this parameter in Eqn. (3) we obtain

$$X_{\text{org}} = (\langle \delta_{\text{carb}} \rangle - \delta_{\text{tc}}) / \Delta, \quad (4)$$

since $\Delta = \langle \Delta \rangle = \langle \delta_{\text{carb}} \rangle - \langle \delta_{\text{org}} \rangle$ where $\langle \Delta \rangle$ is the average Δ -value for this time period.

We measure $\delta^{13}\text{C}$ in carbonate rocks directly (Fig. 3); thus, the δ_{carb} -curve in Fig. 3 represents the instantaneous value for marine carbonate rocks at their time of deposition. We may determine the curve for the average $\delta^{13}\text{C}$ value in the carbonate reservoir ($\langle \delta_{\text{carb}} \rangle$) by integrating the δ_{carb} curve from Fig. 3 using the following mass balance equation:

$$\tau_{\text{carb}} \frac{d\langle \delta_{\text{carb}} \rangle}{dt} = [\delta_{\text{carb}} - \langle \delta_{\text{carb}} \rangle] \quad (5)$$

where τ_{carb} is the residence time of C in the carbonate reservoir and is, in general, a function of time. In deriving Eqn. (5) we assumed that new additions to the carbonate reservoir

are always given by the δ_{carb} curve and that carbonate of average isotopic composition is removed by erosion from the carbonate reservoir. Because we do not a priori know the value of τ_{carb} , we vary this parameter over a likely range. The secular trends in Fig. 4 were calculated using values of $\tau_{\text{carb}} = 100, 250$ and 500 Ma. The extremes likely represent the probable limits of τ_{carb} and the value of 250 Ma was suggested by VEIZER (1988). Using Eqn. (4) these trends can be exactly related to secular trends in the mass fraction of organic C (X_{org}) as a function of time (Fig. 4). Because of the much longer residence time of C in sediments, the strong variations in $\delta^{13}\text{C}$ in the Late Proterozoic oceans are damped in the average value of the sedimentary mass. The value of $\langle \delta_{\text{carb}} \rangle$ responds about three orders of magnitude more slowly to changing carbon fluxes out of the oceans than does δ_{carb} .

CAUSES OF VARIATIONS OF SEAWATER $^{87}\text{Sr}/^{86}\text{Sr}$ AND $\delta^{13}\text{C}$

The evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater is dominated by the change in the ratio of the subaerial weathering flux of Sr (J_{rw}) from land masses and the submarine weathering flux of Sr (J_{hw}) from hydrothermal alteration of oceanic crust. Not only do the relative mass fluxes of Sr vary in these two components, but the isotopic composition of each can vary as well. Consequently, the Sr isotopic record of seawater alone does not uniquely constrain the flux ratio of river water to hydrothermal fluid. GOLDSTEIN and JACOBSEN (1988) have shown that ϵ_{Nd} is correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ in river water. With this correlation, we can use the ϵ_{Nd} curve for seawater to constrain the Sr flux ratio through time (JACOBSEN, 1988).

If the Sr flux curve primarily reflects changes in erosion, then the erosion time parameter k_{Sr} (= inverse value of the residence time of Sr in the sedimentary reservoir) can be directly related to their $J_{\text{rw}}/J_{\text{hw}}$ flux ratio curve. If we assume a constant mass of Sr in the sedimentary reservoir over this time, and further, that the fraction of Sr transported in dis-

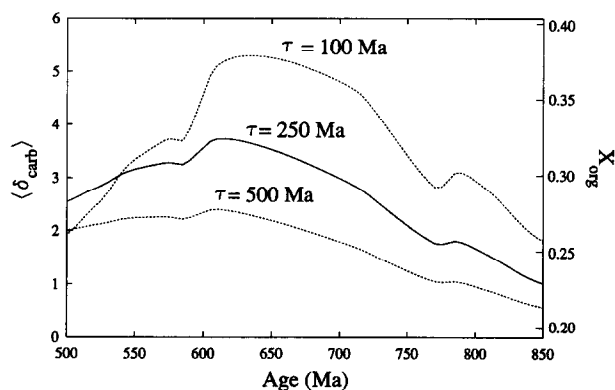


FIG. 4. Secular variations in the $\delta^{13}\text{C}$ value of the average carbonate reservoir ($\langle \delta_{\text{carb}} \rangle$) and the mass fraction of carbon preserved as organic carbon (X_{org}) in the sedimentary reservoir through the Late Proterozoic. The $\langle \delta_{\text{carb}} \rangle$ curve is calculated by integrating the marine carbonate curve in Fig. 3 (see Eqn. 5). The magnitude of these changes is related to the residence time (τ) of carbon in the average carbonate reservoir. We vary this parameter over a likely range between 100 to 500 Ma. Shorter residence times yield greater variation, yet overall trends remain the same.

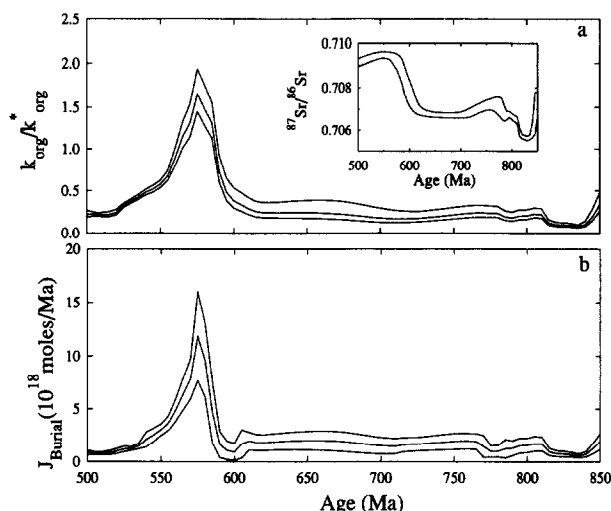


FIG. 5. (a) Secular variations in the global erosion rate of organic carbon (k_{org}) relative to the present-day rate (k_{org}^*). This curve was obtained from the Sr flux curve of ASMEROM et al. (1991). The value k_{org} is proportional to the river water to hydrothermal water flux ratio for Sr [thus, $k_{\text{org}}/k_{\text{org}}^* = (J_{\text{rw}}/J_{\text{hw}})/(J_{\text{rw}}^*/J_{\text{hw}}^*)$] determined by secular variations in the strontium (see insert) and neodymium isotope curves (see ASMEROM et al., 1991). (b) Secular variation in the organic carbon burial flux (J_{burial}) through the Late Proterozoic. For comparison, the present-day value for J_{burial} is estimated at 3.8×10^{18} mol/Ma. The calculated curves suggest that organic carbon burial was low throughout most of the Late Proterozoic until about 600 Ma when J_{burial} rose sharply to 2–4 times the modern rate and then decreased rapidly into the Cambrian.

solved relative to particulate matter in rivers does not change substantially, then it follows that

$$F_{\text{Sr}}(t) = k_{\text{Sr}}(t)/k_{\text{Sr}}^* = \frac{J_{\text{rw}}(t)/J_{\text{hw}}(t)}{J_{\text{rw}}^*/J_{\text{hw}}^*} \quad (6)$$

where the asterisk (*) denotes the present-day values. To couple the Sr and C cycles, we have chosen to assume that k_{org} is proportional to the erosion time parameter for Sr. Thus, we obtain

$$k_{\text{org}}(t) = k_{\text{Sr}}(t)(k_{\text{org}}^*/k_{\text{Sr}}^*) = F_{\text{Sr}}k_{\text{org}}^* \quad (7)$$

ASMEROM et al. (1991) recalculated $J_{\text{rw}}/J_{\text{hw}}$ for the period from 900 Ma to 500 Ma based on their new seawater Sr isotopic evolution curve shown in the inset in Fig. 5a. The curve shows relatively low values of $J_{\text{rw}}/J_{\text{hw}}$ through 600–800 Ma and a rapid increase in $J_{\text{rw}}/J_{\text{hw}}$ after the Varangian (ca. 590–610 Ma) which almost certainly reflects elevated erosion rates associated with the Pan-African Orogeny (JACOBSEN, 1988; ASMEROM et al., 1991). This curve is used as an estimate of $k_{\text{org}}/k_{\text{org}}^*$ (using 6 and 7) which is shown in Fig. 5a. This is valid since for most of this time the Sr flux curve appears to primarily reflect changes in continental erosion rates (ASMEROM et al., 1991). However, the inference of high values of J_{hw} during 800–850 Ma implies that erosion rates calculated using this method could be somewhat low during that time (VEIZER et al., 1983; JACOBSEN and PIMENTEL-KLOSE, 1988; ASMEROM et al., 1991).

Changes in the mass of the organic C reservoir primarily reflect a balance between the rate of burial of organic C (J_{bur})

and the rate of erosion of organic C in sediments (J_{er}). Thus, the change in M_{org} with time is given by

$$\frac{dM_{org}}{dt} = J_{bur} - J_{er}. \quad (8)$$

To a first approximation, if we can constrain the erosional flux (J_{er}) and the rate of change of the organic C reservoir (dM_{org}/dt) through time, we can obtain the burial rate of organic C as a function of time. We assume that the erosion rate of carbon is proportional to the total amount of C in the organic reservoir (i.e., that the erosion process is first order). Thus,

$$J_{er} = k_{org} M_{org} \quad (9)$$

where k_{org} is the erosion time parameter for organic carbon. k_{org} is in general a function of time, so combining Eqns. (7), (8), and (9) we obtain

$$\frac{dM_{org}}{dt} = J_{bur} - F_{Sr} k_{org}^* M_{org}. \quad (10)$$

If we introduce X_{org} (from Eqn. 2) into Eqn. (10) and solve for the burial rate of organic carbon, we obtain an equation with quantities we obtain from the isotopic mass balance:

$$J_{burial} = M_{tc} \left(F_{Sr} k_{org}^* X_{org} + \frac{dX_{org}}{dt} \right). \quad (11)$$

It follows from the C-isotopic mass balance (Eqn. 4) that for a constant Δ value that

$$\Delta \frac{dX_{org}}{dt} = \frac{d\langle \delta_{carb} \rangle}{dt}. \quad (12)$$

Finally, using Eqns. (4) and (12) we can rewrite Eqn. (11) as

$$J_{bur} = \frac{M_{tc}}{\Delta} \left[F_{Sr} k_{org}^* (\langle \delta_{carb} \rangle - \delta_{tc}) + \frac{d\langle \delta_{carb} \rangle}{dt} \right] \quad (13)$$

and solve for J_{bur} as a function of time (Fig. 5b).

If $\tau_{carb} = \tau_{org} = 1/k_{org}$ then by using Eqn. (5), Eqn. (13) simplifies to

$$J_{bur} = \frac{M_{tc}}{\Delta} k_{org}^* F_{Sr} (\delta_{carb} - \delta_{tc}) \quad (14)$$

where $k_{org}^* = 0.004 \text{ Ma}^{-1}$, $\Delta = 28.5$, $M_{tc} = 6250 \cdot 10^{18} \text{ mol}$ (LASAGA et al., 1985) and $\delta_{tc} = -5.5\text{‰}$. Thus, $M_{tc} k_{org}^* / \Delta = 0.88 \cdot 10^{18} \text{ mol/Ma}$ and $J_{bur} (10^{18} \text{ mol/Ma}) = 0.88 F_{Sr} (\delta_{carb} + 5.5\text{‰})$.

DISCUSSION AND CONCLUSIONS

Variations in Organic C Burial and Hydrothermal Activity

The prolonged period of deposition of ^{13}C -enriched marine carbonates during the late Riphean and Vendian indicates substantial shifts in the mass balance between organic and carbonate C in the marine environment (KNOLL et al., 1986; STRAUSS et al., 1992). This extended period of ^{13}C -enriched carbonates resulted from a substantial shift in the distribution of reduced and oxidized carbon in the sedimentary reservoir, yielding high values of X_{org} (Fig. 4). Using the model above,

we have calculated the burial rates of organic carbon necessary to produce these shifts (Fig. 5b). Because of the dependence of C_{org} burial rates on the overall erosion rate, the calculated pattern of C_{org} burial rates shows important differences from the $\delta^{13}\text{C}$ -curve of marine carbonates (Fig. 3). High $\delta^{13}\text{C}$ values in marine carbonates indicate high fractional burial rates of C_{org} , but do not necessarily imply high overall burial rates. Throughout most of the late Riphean, the calculated burial flux of organic C is about $2 \times 10^{18} \text{ mol/Ma}$, significantly less than the present-day value of $3.8 \times 10^{18} \text{ mol/Ma}$ (LASAGA et al., 1985). Thus, during the late Riphean very high X_{org} values are not associated with high C_{org} burial fluxes.

Characteristically low $^{87}\text{Sr}/^{86}\text{Sr}$ values from the late Riphean indicate moderate erosion rates and increased submarine hydrothermal activity (DERRY et al., 1989; ASMEROM et al., 1991). Further evidence for hydrothermal activity comes from the widespread occurrence of banded iron-formations (BIFs) in late Riphean sediments (Fig. 6). A number of studies have demonstrated that submarine hydrothermal systems supply an important fraction of the components of BIFs (JACOBSEN and PIMENTEL-KLOSE, 1988; BARRET et al., 1988; KLEIN and BEUKES, 1989; DERRY and JACOBSEN, 1990). While the age constraints on some Late Proterozoic BIFs are not tight, it appears that BIF deposition, frequent during the late Riphean, had ceased by the time of Varangian glaciation. This pattern coincides closely with the isotopic evidence for the sources of Sr in seawater. BIFs were deposited when $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater was low, and disappear when $^{87}\text{Sr}/^{86}\text{Sr}$ values began to rise rapidly at the start of the Vendian. Thus, Varangian time (ca. 600 Ma) appears to mark an im-

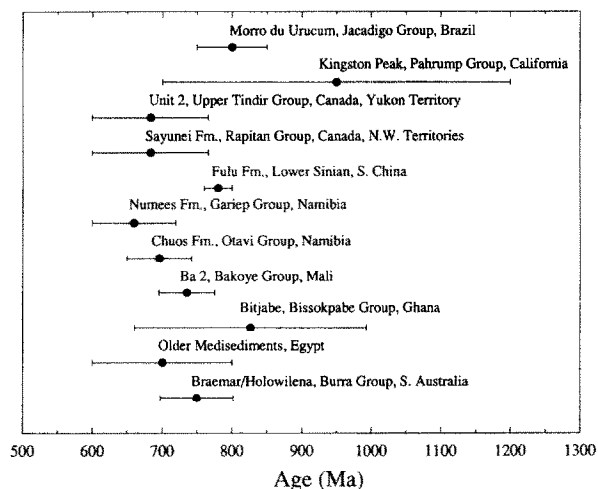


FIG. 6. Occurrences and known age ranges of Late Proterozoic iron formations in Brazil (DORR, 1973; HOPPE et al., 1985), USA (YEO, 1981), Canada (EISENBACHER, 1978; YOUNG, 1976, 1982; YEO, 1981), South China (SHIH-FAN, 1981; YUELUN et al., 1981), Namibia (HEDBERG, 1979), Mali (CLAUER et al., 1983; CLAUER and DEYNOUX, 1987; GIRARD et al., 1989), Ghana (TROMPETTE, 1981), Egypt (STERN and HEDGES, 1985), and Australia (COMPSTON et al., 1966; COATS and PREISS, 1980; COATS, 1981; COSTA et al., 1983; FANNING et al., 1986). Age ranges indicate that all Late Proterozoic iron formations predate 600 Ma suggesting that the hydrothermal flux rate of iron was likely high through parts of this period and then decreased substantially sometime before the Varanger glacial episode.

portant change in the behavior of the exogenic cycle. Both C and Sr isotope curves change markedly at this time, and a conspicuous member of sedimentary sequences disappears from the record.

Mechanism For Large ^{13}C Enrichments

We now consider some possible mechanisms for producing the large enrichments in $\delta^{13}\text{C}$ in Late Proterozoic carbonates and organic C. Two points must be kept in mind. First, in the absence of a significant terrestrial biomass, the locus of organic C burial may have been different from the present day, with less burial in deltaic sediments. Second, the absence of bioturbation facilitated the preservation of sedimented organic matter. The degree of preservation of organic matter in clastic sediments depends chiefly on three processes:

- (1) High sedimentation rates promote C_{org} preservation by rapidly burying organic matter below the oxic zone in the sediment column (BERNER and CANFIELD, 1989).
- (2) High productivity, stimulated by nutrient supply, increases the flux of organic carbon to the sediments (FROELICH et al., 1982).
- (3) An anoxic water column above the sediment-water interface retards oxidation of settling organic matter.

The time scale of these processes and relations between the Sr and C records shed some light on which of these possibilities was likely to have been important. Prior to the dramatic increase in $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater at around 600 Ma, the evidence from the Sr isotopic record indicates relatively low erosion rates, and hence low sedimentation rates (ASMEROM et al., 1991). This demonstrates that the positive values of $\delta^{13}\text{C}$ in late Riphean sediments were not produced by unusually rapid global sedimentation rates. A prolonged period of high marine productivity is even less likely as nutrients in the ocean would be exhausted on a short time scale. For example, the residence time of P in the oceans is on the order of 10^5 years, while the late Riphean C excursion is on the order 2×10^8 years duration. The C-P system has a negative feedback such that burying organic matter also sequesters P, thereby effectively limiting increases in productivity (HOLLAND, 1978; BROECKER and PENG, 1982). The presence of BIFs in late Riphean sedimentary sequences suggests that hydrothermal Fe was another significant sink for P. The precipitation of hydrothermally supplied Fe hydroxides is an important scavenging mechanism for marine P (FROELICH et al., 1982; SHERWOOD et al., 1987). These P sinks, coupled with relatively sluggish erosion rates (the primary source of P to the oceans), make it unlikely that productivity was high during most of the late Riphean.

Extensive and prolonged marine anoxia seems necessary to account for the late Riphean C isotope record. Other lines of evidence, including the sedimentary S isotope record, support this view (HAYES et al., 1992; LAMBERT and DONNELLY, 1992). The apparent bias of $\delta^{34}\text{S}$ in coeval sedimentary sulfides toward heavy values suggests that the "missing" light S may have been precipitated as sulfides in deep water. The hydrothermal flux of reduced species, such as H_2S , Mn^{2+} , Fe^{2+} , and CH_4 , probably contributed significantly to deep-water anoxia. The juvenile flux of CO_2 associated with sub-

marine volcanic activity could also have forced compensation by the C cycle. ARTHUR et al. (1985) emphasize the role of juvenile CO_2 in contributing to enhanced C_{org} burial rates in the Cretaceous.

The two strong negative excursions in the Late Proterozoic C isotope record are coincident with the Sturtian and Varangian glacial events (KNOLL et al., 1986). KAUFMAN et al. (1991) suggested that Late Proterozoic glacial events resulted in overturn of a formerly stagnant water column. This turnover would have (1) brought "aged" and ^{13}C -depleted dissolved inorganic carbon from the deep ocean onto shallow carbonate platforms and (2) ventilated the deep ocean, thus removing the anoxic conditions which favored preservation of organic matter. KNOLL et al. (1986) and KASTING (1987) have speculated that the increased burial of organic matter in the Late Proterozoic resulted in lowered CO_2 levels in the atmosphere and thereby contributed to global cooling and the onset of glacial activity. A similar relation between organic matter burial, CO_2 and cooling, the "Monterey event," has been suggested to act in the same fashion during the Miocene (VINCENT and BERGER, 1985). Whatever the exact cause, these excursions represent brief periods of sharply reduced burial of organic C.

The return to high $\delta^{13}\text{C}$ values (+4 to +8‰) in the Vendian above Varangian strata is coeval with the rapid rise in $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 3, insert in 5a). The increase in erosion rate along with the high fractional rate of C_{org} burial at this time result in rapid overall burial rates for organic C. Both the Sr data and the disappearance of BIFs indicate that the role of hydrothermal fluids in controlling marine chemistry was far less important after 600 Ma. The prolonged period of marine anoxia may have been terminated by Varangian events. The sharp but relatively short excursion of high $\delta^{13}\text{C}$ values at about 580 Ma was primarily driven by rapid global sedimentation rates, and also enhanced productivity in the oceans. The inferred supply of P from increased erosion, particularly of young, P-rich sediments, and the diminished importance of hydrothermal Fe as sink for P are consistent with this mechanism. Large phosphorite deposits stratigraphically above Varangian beds are known from numerous locations worldwide (COOK and SHERGOLD, 1986). Thus, the mechanisms responsible for the high $\delta^{13}\text{C}$ values in pre-Varangian sediments appear to differ fundamentally from those which produced the same effect in post-Varangian rocks. Whatever the precise mix of causes, much higher burial fluxes of organic carbon are indicated in the lower Vendian relative to the late Riphean (Fig. 5b). These fluxes are of the same order as those calculated for the Carboniferous-Permian, the time of greatest organic C burial in the Phanerozoic (BERNER and RAISWELL, 1983; HOLSER et al., 1989).

Implications For Environmental Changes

The results of our calculations of the sedimentary C cycle have important environmental implications. Shifts in the mass balance between the organic and carbonate C reservoirs liberate or consume O_2 by schematic reactions such as $\text{CH}_2\text{O} + \text{O}_2 = 2\text{H}^+ + \text{CO}_3^{2-}$. The accumulation of anomalous quantities of organic C in Late Proterozoic sediments implies the release of substantial quantities of O_2 to the hydrosphere. In

their study, KNOLL et al. (1986) calculated an O_2 flux of 4×10^{18} mol/Ma during the late Riphean and Vendian periods. However, their calculation was based on the assumption that the total C flux to the sedimentary reservoir was equal to the modern day fluxes, which as we show (Fig. 5) is not the case for most of the time under consideration. In contrast, our calculations indicate an average flux of ca. 2×10^{18} mol/Ma for the late Riphean, and this O_2 flux to the hydrosphere could well have been balanced by other redox reactions involving C, S, Fe, and Mn.

During the Phanerozoic, shifts in the mass balance of sedimentary C have apparently been compensated by corresponding shifts in the mass balance of sedimentary S (HOLLAND, 1973; GARRELS and PERRY, 1974). This coupling of the sedimentary C and S systems results in an inverse correlation of $\delta^{34}S$ values in sulfates with $\delta^{13}C$ values in carbonates (VEIZER et al., 1980). This mechanism appears to have buffered O_2 levels to close to present-day levels throughout most of the Phanerozoic (GARRELS and LERMAN, 1984; HOLLAND, 1984). Variations in atmospheric pO_2 of up to 50% may have occurred when imbalances developed in the C-S system (SCHIDLOWSKI and JUNGE, 1981; KUMP and GARRELS, 1986; BERNER and CANFIELD, 1989; LASAGA, 1989). While the record of $\delta^{34}S$ from Late Proterozoic sulfates is sparse, it appears uncorrelated with $\delta^{13}C$ values in coeval carbonates (LAMBERT et al., 1987; HAYES et al., 1992). This implies that the S cycle did not act to balance O_2 fluxes out of the C cycle by large-scale precipitation of sulfate. Low erosion rates in the late Riphean suggest that the weathering sink for O_2 was also less important than at present. However, some mechanism to limit atmospheric O_2 concentration is required in order to keep O_2 levels within reasonable bounds (e.g., KNOLL et al., 1986; STRAUSS et al., 1992). The presence of large BIFs from this interval suggests that hydrothermal fluids rich in reduced Fe, Mn, and H_2S were an important O_2 sink (DERRY and JACOBSEN, 1988). As discussed earlier, the isotopic record of Sr supports the existence of significant hydrothermal fluxes into the oceans prior to Varangian time. Simple calculations of the hydrothermal mass flux of Fe required to form large BIFs provide a broad constraint on the potential hydrothermal flux (DERRY and JACOBSEN, 1990). When combined with the associated Mn and H_2S fluxes known in modern and experimental hydrothermal fluids, the O_2 demand of this system is quite significant. Using the concentrations of H_2S , Fe, and Mn determined experimentally in hydrothermal fluids at 400°C by SEEWALD and SEYFRIED (1990), we obtain a total O_2 -demand of about 3×10^{-5} mol/g. Thus, with a hydrothermal water flux of 10^{17} g/yr (cf. PALMER and EDMOND, 1989), the hydrothermal systems have an O_2 -demand of 3×10^{18} mol/Ma. While this calculation cannot be taken as proof of the role of hydrothermal fluids, it does illustrate the possible importance of this mechanism. In principle, most or all of the O_2 -flux out of the C system prior to the Varangian event could have been buffered by the submarine hydrothermal flux. We propose that the oxidation of hydrothermal fluids, along with weathering reactions, effectively limited buildup of atmospheric O_2 prior to about 600 Ma.

The situation changes significantly around the Varangian glaciation. Initially, organic C burial rates drop significantly. However, both C_{org} burial rates and the river water/hydro-

thermal flux ratio increase rapidly after the negative excursion (Fig. 5a). Thus, the very high C_{org} burial rates after the Varangian occur at a time when the flux of reduced hydrothermal fluids to the hydrosphere had fallen considerably. The large fluxes of O_2 out of the C system at this time were apparently not balanced by the O_2 demands of submarine hydrothermal fluids, and there is no geologic or isotopic evidence for widespread sulfate burial. The combination of rapid C_{org} burial rates and lowered Fe-Mn-S fluxes from the mantle provide a mechanism for rapidly increasing levels of atmospheric O_2 . Thus, while the function of the exogenic cycle does not appear to require significant changes in pO_2 in the late Riphean, the lower Vendian appears to be a time of major increase in pO_2 . What role the S cycle may have played in establishing O_2 levels is not yet clear. Certainly other O_2 sinks were important, particularly weathering of the crust. An indication of the importance of weathering as an O_2 sink is given by the decrease in the X_{org} value of the integrated carbonate reservoir at this time (Fig. 4). This implies that the sedimentary C reservoir was acting as a net sink for O_2 . Without better knowledge of weathering rates or S-isotopic distributions we cannot calculate the net O_2 gain by the hydrosphere. However, the O_2 capacity of the C cycle is such that O_2 levels in the atmosphere could have risen from very low levels to as high as, or possibly even higher than the present day in as little as ten million years. Rapid erosion promoted oxidative weathering as the principal O_2 sink at this time. Rising atmospheric O_2 levels may also have been affected by negative "oxygen feedback" on weathering rates (see discussion in HOLLAND, 1978; BUDYKO et al., 1987; BERNER and CANFIELD, 1989; LASAGA, 1989).

The implications of such a sudden rise in atmospheric pO_2 for evolutionary processes are considerable. CLOUD (1976) first suggested that Late Proterozoic metazoan evolution may have been triggered by rising oxygen concentrations. The correspondence between the geochemical events we have described above and the paleontological record in the Vendian is an intriguing test of that hypothesis. Fossils of Ediacaran-type animals and some of the earliest known biomineralizing metazoans have been recognized from some of the same sequences (Nama Group) we have used to define the high burial rates of organic C and high erosion rates. The Nama Group also contains some of the earliest known calcareous algae, as do possibly coeval facies from Siberia (RIDING and VORONOVA, 1984; GRANT et al., 1991). As RUNNEGAR (1982) and HOLLAND (1984) have pointed out, the existence of these phyla sets lower limits on pO_2 , but does not by itself set an upper limit. However, if metazoan evolution was in some way a response to changing environmental factors such as pO_2 , this analysis suggests that the response was rapid, at least on a geologic time scale.

Acknowledgments—This work was supported by NSF grant EAR-8904693 to S. B. Jacobsen and the Edward Mallinckrodt Jr. Memorial Fund of the Department of Earth and Planetary Sciences at Harvard University. We thank A. H. Knoll, G. J. B. Germs, P. N. Southgate, and D. J. DesMarais for providing some of the samples used in this study. We thank J. Veizer and D. J. DesMarais for helpful comments on this paper.

Editorial handling: S. R. Taylor

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