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Carbon isotopic record of the latest Proterozoic from Oman

By STEPHEN J. BURNS and ALBERT MATTER [1]

ABSTRACT

The carbon isotopic ratios of marine carbonate rocks from the latest Precambrian to possibly earliest Cambrian were studied to evaluate possible changes in organic carbon burial and hence in the carbon cycle associated with the evolution of higher life forms. Samples were taken from carbonate units within the Huqf Group of Oman, which was deposited during the interval from approximately 560 to 540 Ma. The data show an initial period of positive $\delta^{13}C$ values, around + 4‰ PDB, followed by a sharp decrease, over a few meters of section, of about 8‰ in carbon isotopic values, to inferred oceanic carbon values of appoximately – 4‰ PDB. The $\delta^{13}C$ values then more slowly increase to between 0 and + 2‰. This isotopic pattern may be correlated across Oman over a distance of 800 km. Similar changes have been observed in Namibia, Greenland and Siberia. The changes are thought to be primarily an original oceanic signal, and not a diagenetic one. The data indicate a sudden significant reduction in organic carbon burial rates in the late Vendian, followed by a slow return to more normal conditions by the end of the Proterozoic. These large changes in the carbon cycle shortly before the Precambrian/Cambrian boundary may have triggered or favored the radiation of metazoan life.

ZUSAMMENFASSUNG

Die Kohlenstoff-Isotopenverhältnisse mariner Kalke und Dolomite des späten Präkambriums bis frühesten Kambriums wurden untersucht um abzuklären, inwieweit Veränderungen der globalen Sedimentationsrate von organischem Material und somit des Kohlenstoffkreislaufes mit der Entwicklung höheren Lebens in Zusammenhang stehen könnten. Die Karbonatproben stammen aus Profilen der Huqf Gruppe im Sultanat Oman, welche den Zeitabschnitt von ca. 560–540 Ma umfasst.

Die Messresultate zeigen im unteren Abschnitt der Profile zunächst relativ konstante positive $\delta^{13}C$ Werte um + 4‰ PDB, gefolgt von einer abrupten Abnahme auf – 8 bis – 12‰ PDB. Dies entspricht nach Berücksichtigung des Diageneseeffekts einem $\delta^{13}C$ Wert des gelösten anorganischen Kohlenstoffs im damaligen Ozean um – 4‰. Gegen das Hangende verändert sich das Kohlenstoff-Isotopenverhältnis sodann langsam zu schwereren Werten auf 0 bis + 2‰. Dieses isotopische Muster kann in Oman über annähernd 800 km korreliert werden; ähnliche Trends sind auch in spätpräkambrischen Serien weitentfernter Gebiete wie etwa Namibia, Grönland und Sibirien festgestellt worden. Die beobachteten Veränderungen des Kohlenstoff-Isotopenverhältnisses stellen primär ein ozeanisches und nicht ein diagenetisches Signal dar. Sie widerspiegeln eine plötzliche bedeutende Abnahme der globalen Sedimentationsrate des organischen Materials im späten Vendian, möglicherweise infolge stark reduzierter Produktivität, gefolgt von einem langsamen Anstieg zu normalen Bedingungen am Ende des Präkambriums. Dieses einschneidende Ereignis im Kohlenstoffkreislauf kurz vor der Wende vom Präkambrium zum Kambrium könnte die Entwicklung der Metazoen ausgelöst oder begünstigt haben.

Introduction

Temporal variation in the carbon isotopic composition of marine carbonates generally reflect isotopic changes in the dissolved inorganic carbon in the oceans (Veizer et al.

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1980; Lindh et al. 1981). Observed changes have been used to infer changes in the global carbon cycle (Garrels and Lerman 1984; Berner 1987) and to identify changes in oceanic productivity associated with mass extinction events (Magaritz 1987; Holser et al. 1991). A number of recent studies have focused on geochemical signals in Late Precambrian to Early Cambrian carbonates (Tucker 1986; Magaritz et al. 1986; Knoll et al. 1986; Aharon et al. 1987), during the time in which macroscopic metazoan life evolved (Stanley 1976). These studies have generally had two goals in mind, to use the pattern of isotopic changes as stratigraphic markers, and to discover the geochemical environment in which complex metazoan life evolved.

In studies which have focused on isotopic events below the Precambrian/Cambrian boundary, rocks from several different late Precambrian basins show the similar types of carbon isotope changes. Generally positive late Precambrian carbon isotopic values are punctuated by one or more relatively large, sharp negative excursions in $\delta^{13}C$ (Knoll et al. 1986; Knoll 1990; Kaufman et al. 1990; Derry et al. 1992). The precise nature and timing of the latter event or possibly events is still not certain. It is important, therefore, to develop further detailed records of carbon isotope changes in the late Precambrian. Such records will help determine whether isotope events are correlable. They will also serve to further refine the timing and magnitude of these events, and associated changes in the carbon cycle, with respect to evolutionary changes.

We report here on a study of carbon isotopes of a relatively well-dated, continuous sequence of Late Proterozoic (c. 560–540 Ma) sedimentary rocks from Oman, the Huqf Group. The rocks are the oldest sedimentary unit in Oman, overlie well-dated basement rocks, and are generally not significantly affected by diagenesis. The Huqf thus provides an excellent opportunity to investigate oceanic carbon isotope changes during the latest Precambrian.

Stratigraphy

As presently defined, the Huqf Group consists of five formations resting directly on volcanic extrusives and igneous basement (Gorin et al. 1982; Hughes Clarke 1988). It is a total of approximately 1500 m thick in central and southern Oman, and is little tectonized and unmetamorphosed (Gorin et al. 1982).

For the present study, samples were taken from carbonate units in the upper four formations of the Huqf Group (Figs. 1 and 2) from central and southern Oman, and from equivalent rocks in the Oman Mountains (Rabu 1988). The first of these, the Khufai Formation, consists of dark bituminous dolomites overlain by dolomitized peritidal carbonates. The latter include shallow water grainstones and algal-laminated micrites. The transition from the Khufai to the shallow water siltstones and shales of the overlying Shuram Formation is very sharp in the Huqf area, with a hardground surface formed on top of the Khufai, but is transitional over a few meters in the subsurface (Hughes Clarke 1988). The lower portions of the Shuram are shallow water marine siltstones with a few interbedded oolitic limestones. The siltstones grade upward into deeper water shales and shaley limestones, and gradually pass into thickly bedded shallow water cabonates of the Buah Formation. The Buah consists largely of stromatolitic dolomicrites, with dolomitized grainstones. It is overlain by an evaporite unit, the Ara Salt, which includes a number of interbedded dolomite layers.

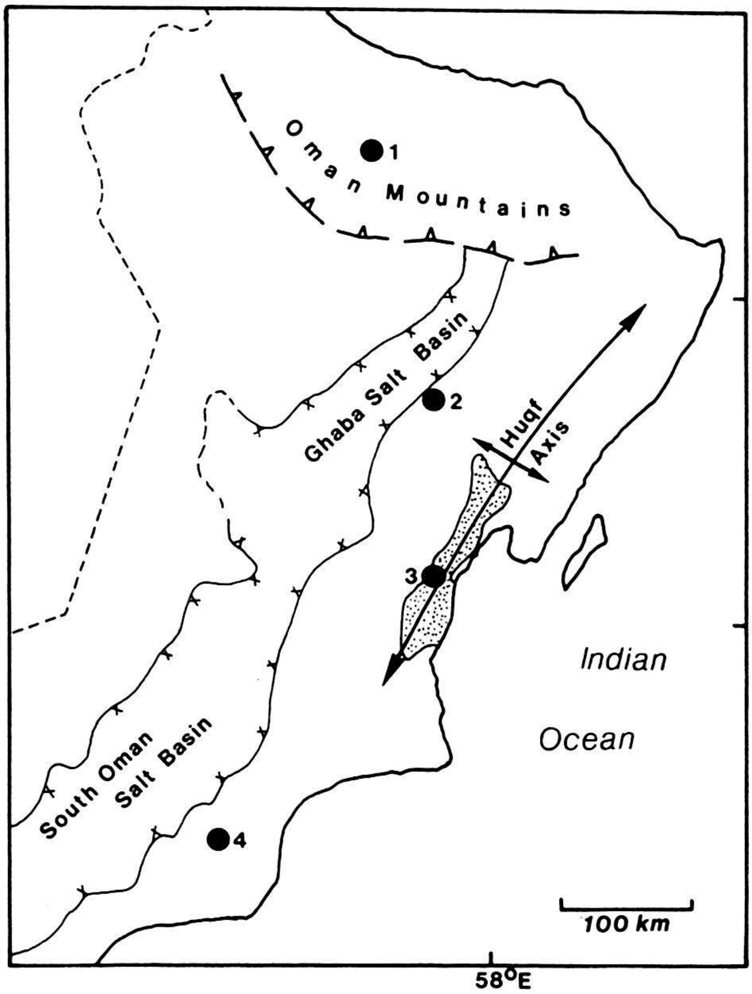

Fig. 1. Location map of studied sections and lithologic columns for central Oman area and the Oman Mountains. Closed circles mark the locations of the four sections studied: 1. Outcrops from the Jebel Akhdar in the Oman Mountains, 2. Well MQ from the flank of the Ghaba Salt Basin, 3. Outcrops from the Huqf Area in central Oman and 4. Well T from the flank of the South Oman Salt Basin.

The correlative sequence of rocks in the Oman Mountains is similar to the Huqf Group in lithology and depositional environments (Rabu 1988), with two major differences. First, the lower carbonate unit is undolomitized. Second, all the formations in the Oman Mountains sustained low grade metamorphism (Hughes Clarke 1988; Rabu 1988) during overthrusting of the Semail ophiolite.

The depositional ages of the Huqf Group are relatively well constrained as compared to most sections of Late Proterozoic rocks. New dates on volcanic and intrusive rocks underlying the Huqf Group in central and southern Oman provide a good lower absolute age limit on deposition. Ignimbrites and granites, both dated by ^{87}Rb/^{87}Sr, from below the Abu Mahara Formation were emplaced at 554 ± 10 Ma (Dubreuilh et al., 1992). Thus, Huqf deposition could not have begun much earlier than 560 Ma.

The upper age limit of the Huqf Group is approximately the age of the Precambrian/Cambrian boundary. The Ara Salt contains two of the few useful biostratigraphic fossils in the Huqf, the tubular calcareous organism *Cloudina spp.* and *Angulocellularia spp.* Our own work and that of Conway Morris et al. (1990) have found *Cloudina* in carbonate

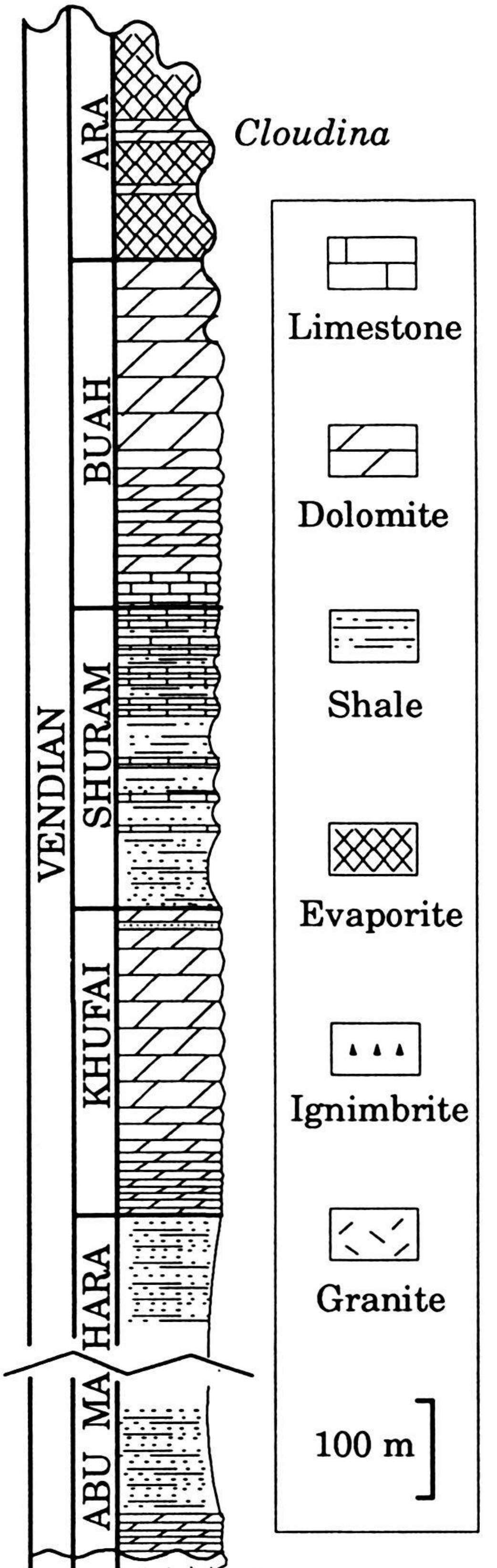

Fig. 2. Stratigraphy of the Huqf Group for central and southern Oman.

beds recovered from boreholes in southern Oman. *Cloudina*, or closely related organisms, have also been reported from a number of other locations worldwide (Grant 1990). It is often associated with an Ediacaran fauna (Grant 1990; Germs 1982) and is found only below unequivocally Cambrian fossils (Grant 1990). Grant (1990) has suggested that *Cloudina* is a useful marker for the terminal Proterozoic. Its presence in the Ara suggest a latest Proterozoic to possibly earliest Cambrian age for that formation. This interpretation is supported by the presence in the Ara of the late Precambrian to early Cambrian calcified alga *Angulocellularia spp.*, and the very high sulphur isotope ratios of Ara evaporites (Mattes & Conway Morris 1990), which are typical of late Precambrian to early Cambrian seawater (Holser 1977). The uppermost age limit for the Huqf is therefore likely to be close to the age of the Precambrian/Cambrian boundary. An absolute age for the boundary, however, has not yet been agreed upon. Estimates range from 600 to 530 Ma, with groups of age data at 570 and 540 Ma (Cowie & Harland 1990). Recent dating of early Cambrian rocks at around 520–525 Ma (Compston et al. 1992; Cooper et al. 1992) and the age of basement in Oman would seem to support a boundary age of around 540 Ma. Thus, we estimate an age of around 540 Ma for the top of the Huqf Group, recognizing that this estimate may be refined as more age data for this time period appear.

Methods

A total of 435 samples from two outcrop sections and two wells were used in the study. All outcrop samples, 148, were studied petrographically, and were analyzed by XRD or staining to determine mineralogy. Petrographic analysis of all samples included study in a standard light microscope, and under blue-fluorescent light. Approximately 40 samples were also studied under cathodoluminescence.

409 samples were analyzed for carbon and oxygen isotope ratios. For the outcrop samples, subsamples free of surface alteration and free of secondary calcite in the form of vein or cavity filling cement were used. The well samples were primarily well-cuttings, with additional side-wall samples to provide stratigraphic control. For all samples, approximately 10 mg of powdered samples was reacted in "100%" H_3PO_4 at 90°C (McCrea 1950) in an on-line automated preparation system. The resulting CO_2 was analyzed on a VG Prism II ratio mass spectrometer. Repeated analyses of standard material show a reproducibility of better than 0.1‰ for $\delta^{18}O$ and less than 0.05‰ for $\delta^{13}C$. All results are presented relative to the PDB standard.

Fortyfive outcrop samples from the Huqf area were analyzed for strontium and manganese contents. The samples were leached for 15 minutes in 1 N HCl, then filtered through 0.45 μm filter paper. The leaches were then analyzed by flame atomic absorption spectroscopy for strontium and manganese.

Results

The carbon isotopic stratigraphy of the four locations studied from Oman show similar major features (Fig. 3). Values for the Khufai Formation are relatively constant positive values of around + 4 ± 2‰ PDB. At the top of the Khufai there is a very sharp drop in carbon isotopic ratios to values from − 8 to − 11‰ PDB. This change occurs over as little as 20 to 30 m of section. Carbon isotopic ratios remain low through most

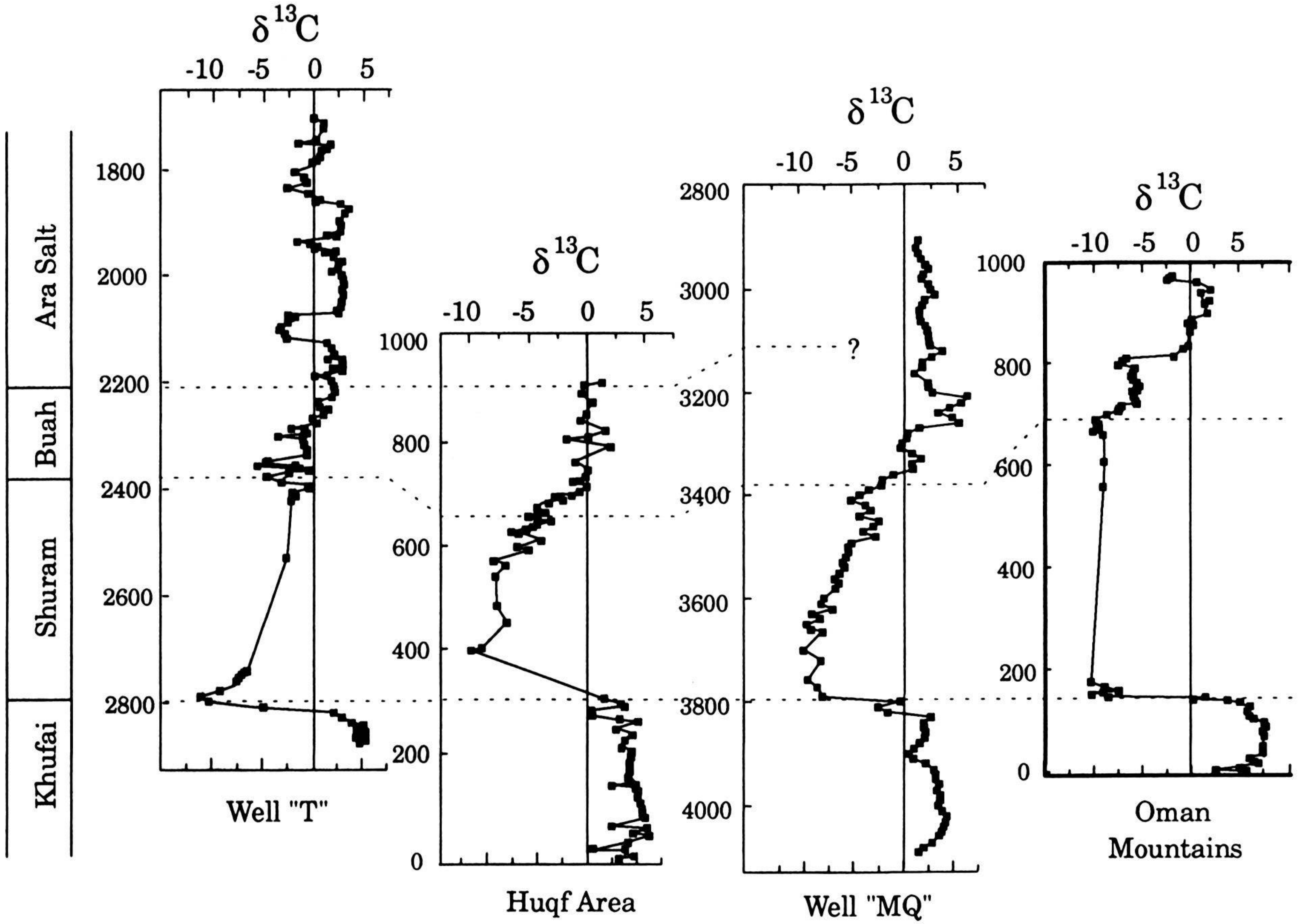

Fig. 3. Carbon isotope data for the four locations in Figure 1. Squares represent individual samples, scales to the left of each section are in meters. All outcrop analyses are from whole rock samples free of obvious late stage cements. Samples from the wells are primarily from cuttings, with a few side wall samples. The well depths are in meters below the surface. The baselines for the outcrop samples from the Huqf area and Oman Mountains are the base of the Khufai Formation.

or all of the Shuram Formation, increasing slightly to values of around − 4 to − 5‰ PDB in the upper parts of the Shuram, where the formation becomes primarily carbonate with fewer interbedded shales. Carbon isotopic ratios continue to increase in the Buah Formation reaching values around 0‰ PDB or slightly above. Values for dolomite units within the Area Salt are generally slightly positive, between 0 and + 2‰, with a few samples having more negative values.

Oxygen isotope ratios do not show any consistent pattern when plotted versus depth (Fig. 4). The values are generally between 0 and − 6‰ except for the Oman Mountains section where the values may be as low as − 13‰. No consistent relationship between $\delta^{13}C$ and $\delta^{18}O$ is observed.

Strontium concentrations of the Huqf area samples are strongly dependent on mineralogy (Fig. 5). Dolomite samples from the Khufai and Buah Formations generally have strontium contents between 30 and 70 ppm, with an average of 45 ppm. The limestone samples from the Shuram and lowermost few meters of the Buah have more variable strontium contents, from 167 to 474 ppm. In the limestones, strontium and $\delta^{13}C$ values are positively correlated (Fig. 5). No correlation between strontium and $\delta^{13}C$ is observed in the dolomites. Manganese contents of both limestones and dolomites are quite variable. The limestones contain from 1509 to 365 ppm Mn with an average of 950 ppm. The dolomites contain from 51 to 2590 ppm with an average of 687 ppm. No covariation of manganese and $\delta^{13}C$ was observed for either limestones or dolomites.

Discussion

The Carbon Isotopic Record of Oman

In estimating the seawater carbon isotope variation it is important to assess to what degree observed variations reflect secular changes in the oceanic carbon reservoir versus postdepositional diagenetic alteration. In general, the Huqf Group of central and southern Oman are good candidates for preservation of the original isotopic values. In the Huqf area the rocks remained a structural high through most of their history and were not subject to major structural deformation (Gorin et al. 1982). The large majority of the samples are non-porous micritic carbonates from nearly pure carbonate units. It is very difficult to alter the carbon isotopic composition of such rocks both of the low porosity and because of the large mass of carbon in the rock itself versus that in any potential diagenetic fluids. Thin sections of samples from the Huqf area often have very well preserved primary features, including stromatolitic laminae, pelloidal textures, radial fabrics in ooids, and intraclastic textures in lime mudstones. Under cathodoluminescence the micritic samples were without exception nonluminescent, which implies a lack of secondary alteration. The fact that a similar isotopic pattern may be correlated 800 km across Oman also suggests that the original pattern of isotopic variations is largely preserved. The isotopic pattern is even present in the Oman Mountains section, where the rocks have a much different diagenetic history, including 8–10 km of burial, low grade metamorphic temperatures and imbricate thrusting and folding.

Other potential indicators of diagenetic alteration are the oxygen and strontium isotopic ratios of the carbonates. In general, the oxygen isotopes show no coherent relationship to the carbon isotope values. The sharp decrease in $\delta^{13}C$ at the top of the

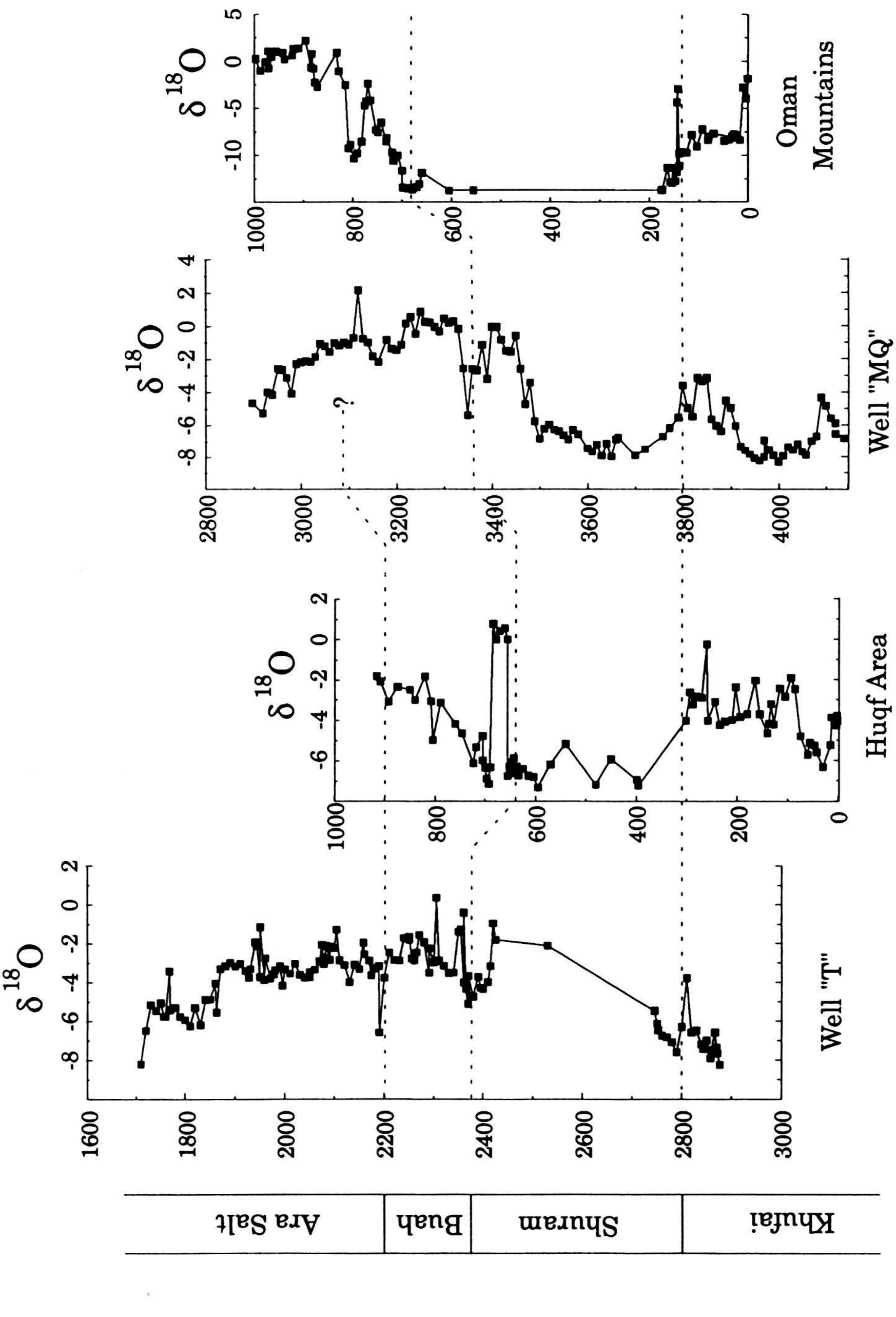

Fig. 4. Oxygen isotope data for the same samples as in Figure 3.

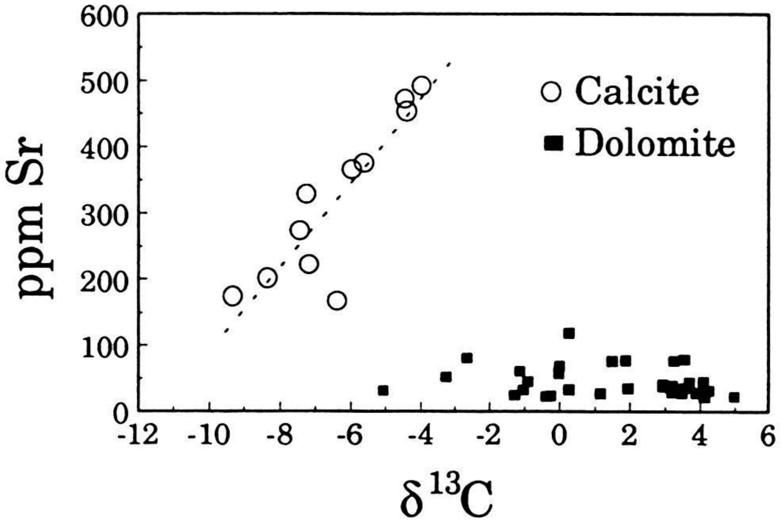

Fig. 5. Crossplot of $\delta^{13}C$ and strontium concentration for outcrop samples from the Huqf area. Correlation coefficient for linear regression of limestone samples, $r^2 = 0.74$.

Khufai Formation is not accompanied by a similar decrease in $\delta^{18}O$. Also, in contrast to the carbon isotopic ratios, the isotopic pattern for $\delta^{18}O$ versus depth varies greatly from one section to another (Fig. 5).

The strontium isotopic ratios of outcrop samples from the Huqf area are reported on in Burns et al. (in press). The ratios show a fairly regular increase from about 0.7084 at the bottom of the Khufai Formation to 0.7091 in the Ara Formation. The values are all within the range found for Phanerozoic marine carbonates. At the very least, the values indicate a rock-buffered diagenetic system as opposed to an open system. In a rock-buffered system the carbon isotopic ratios of carbonate rocks are very likely to be preserved.

The strontium contents of the carbonates are also a means of assessing diagenetic alteration. The dolomites have strontium contents between 30 and 70 ppm (Fig. 5), averaging 48 ppm, values typical of lower Palaeozoic and Precambrian massive dolomites. Vahrenkamp & Swart (1990) recently proposed a strontium distribution coefficient of 0.012 for ordered stoichiometric dolomites. Based on this distribution coefficient, an ordered dolomite in equilibrium with a fluid with the Sr/Ca ratio of modern seawater would contain approximately 50 ppm strontium. The strontium contents of the Huqf dolomites, which are well ordered and near stoichiometric, thus indicate equilibrium with fluids with Sr/Ca ratios close to modern seawater. The strontium contents are thus probably close to their initial values, suggesting preservation of the original dolomite chemistry.

The strontium contents of the limestones are more variable (Fig. 5). The limestones with the lightest carbon isotope values, less than − 4‰ PDB, also have relatively low strontium contents, 173 to 300 ppm. Whereas the limestones with $\delta^{13}C$ values of − 4‰ or higher which contain 400 to 500 ppm strontium. The latter samples, using a strontium distribution coefficient of 0.05 (Lorens 1979; Baker et al. 1982), are approximately in equilibrium with a fluid with a Sr/Ca ratio similar to modern seawater, similar to the dolomites. Again, this suggests a high degree of preservation of the original chemistry of the samples. The limestone samples from the lower half of the Shuram Formation, those with lower strontium contents and the lowest $\delta^{13}C$ values, seem to show evidence of diagenetic alteration. These samples are from thin limestone beds within siltstones and shales, and in some cases contain sparry calcite cements.

The linear relationship between strontium and $\delta^{13}C$ for the limestones (Fig. 5) indicates varying degrees of mixing between diagenetic limestone and original carbonate, and allows an estimation of how much the $\delta^{13}C$ values were altered. The linear covariation suggests that all the limestones initially had $\delta^{13}C$ values around − 4‰. Thus, the magnitude of the negative carbon isotope shift in the world ocean is certainly less than that observed in the Oman sections in which the lowest values, − 10 to − 12‰ PDB, are probably outside of the possible range for dissolved inorganic carbon in the oceans. The ocean carbon isotope record then probably varied as follows: values of around + 4‰ were maintained during deposition of the Khufai formation, the values dropped sharply to approximately − 4‰ during deposition of the Shuram Formation, the values then increased more slowly during deposition of the upper portions of the Shuram and lower portions of the Buah formation to values of around 0 to + 2‰, values which persisted through deposition of the upper portions of the Buah and the Ara Formations.

Other Late Precambrian Carbon Isotope Records

Carbon isotope shifts similar to that observed in Oman may be seen in data from other areas. Both carbonate carbon and organic carbon in Vendian age rocks from Greenland and Norway also show an abrupt shift from heavy to light carbon isotopic ratios (Knoll et al. 1986). Upper Vendian rocks from Siberia also have primarily negative carbon isotopic ratios (Magaritz et al. 1986). The upper portions of the curve seen in Figure 2, the relatively constant values in the Buah and Ara, may not be represented by the Greenland and Norway, or Siberian sections because uppermost Vendian age marine rocks are missing or greatly condensed in those sections (Knoll & Swett 1987; Kaufman et al. 1991). Features similar to the curve from Oman may also be observed in Late Proterozoic rocks from Namibia, including relatively positive values (Zaris Fm.; Schidlowski 1975; Kaufman et al. 1991) followed by a sharp shift to negative values in the overlying rocks (lower Schwarzrand Subgroup; Kaufman et al. 1991), and followed by a return to relatively constant, positive carbon isotopic ratios before the Cambrian/Precambrian boundary (upper Schwarzrand Subgroup of the Nama Group; Kaufman et al. 1991) in rocks which also contain *Cloudina* (Germs 1972).

Precisely how the carbon isotope shifts seen in other basins correlate to the Oman section is problematic. Few late Precambrian sequences are sufficiently well dated to confidently say that only one carbon isotope shift is present, nor to state that a particular carbon isotope shift in one basin correlates to that in another. The absolute age dates of the basement rocks in the Huqf area indicate that the carbon isotope shift in Oman occurred very late in the Precambrian. It appears to be younger than the similar shift observed by Knoll et al. (1986) in Greenland and by Kaufman et al. (1991) in Namibia. The lack of good absolute ages for the shifts from those areas, however, makes any firm statement about possible correlations premature. Knoll (1991) speculated that the late Precambrian oceans generally had quite positive carbon isotope values with several intervals of much lighter values. This remains to be proven, however, and better correlations of the carbon isotope records of various basins will be required before a complete picture of the late Precambrian carbon isotope changes can be drawn.

Causes and Significance of Carbon Isotopic Variation

The cause of the carbon isotopic shifts in the late Vendian ocean are not yet clear. On million year time scales, models of the global carbon system predict a close correspondence between the carbon isotopic composition of inorganic carbon in the oceans (and thus of carbon removed from the ocean as carbonate sediments) and the burial rate of organic carbon (Kump & Garrels 1986; Berner 1987). More precisely, assuming that the isotopic composition of carbon entering the oceans remains relatively constant, the carbon isotopic composition of the marine carbonates will be determined by the relative amounts of carbon ultimately removed to sediments as inorganic versus organic material, with positive values indicating a high percentage of carbon buried as organic material, and vice versa.

The very positive values in the Khufai Formation then correspond to a relatively high percentage of organic carbon burial, and the negative values in the Shuram Formation to a low percentage of organic carbon burial. In fact, mass balance models of the carbon cycle indicate that to lower the isotopic composition of dissolved inorganic carbon in the oceans to values of − 4‰ PDB would require a nearly complete halt to the removal of organic carbon from the ocean (Kump and Garrels 1986; Berner 1987).

The relative amount of carbon removed from the ocean as organic carbon may be in turn affected by several factors, with, for example, high organic carbon burial rates indicating high overall oceanic productivity, widespread anoxia in the oceans, high global sedimentation rates (Berner & Canfield 1989; Derry et al. 1992), or some combinations of these. Derry et al. (1992) suggest that the high $\delta^{13}C$ values observed for post-Varangian marine carbonates were primarily due to high global sedimantation rates and increased productivity which promoted deposition and preservation of deposited organic matter. They based their conclusion mainly on the increasing seawater $^{87}Sr/^{86}Sr$ ratios from which they inferred increasing continental erosion rates and increased sedimentation rates (Derry et al. 1992). The increasing $^{87}Sr/^{86}Sr$ ratios for the Khufai Formation (Burns et al., in press) suggest that similar factors may explain the high $\delta^{13}C$ values during this time period.

The sharp negative excursion at the base of the Shuram Formation is more difficult to interpret. Similar negative carbon isotope excursions have been explained as the result of a change form a poorly-ventilated to a well-ventilated ocean associated with the onset of glaciations (Kaufman et al. 1991; Derry et al. 1992). Renewed more vigorous circulation would result in decreased preservation of organic matter in sediments. No known glacial sediments or period of glacial activity, however, are known to coincide with deposition of the Shuram Formation. The shift to low $\delta^{13}C$ values could also indicate dramatically decreased ocean productivity or sedimentation rates, though there is no direct evidence for either. In any case, the negative values indicate a significant decrease in organic carbon burial rates during this time period.

The timing of the late Precambrian carbon isotope changes with respect to the evolution of specific groups of organisms has yet to be worked out in detail. If *Cloudina* is associated with the Ediacaran fauna and thus approximately equivalent in time to the arrival of the earliest metazoans, then the sharp negative carbon isotope shift, which occurs below the occurrence of *Cloudina* in Oman, may record a global environmental change closely associated with the metazoan radiation.

Knoll (1991) suggested that the generally positive carbon isotope values observed in late Precambrian carbonates are evidence of high oceanic productivity and increasing atmospheric oxygen levels. An increase in atmospheric oxygen has been proposed as a necessary precursor to the late Precambrian/early Cambrian radiation of animals (Towe 1981; Knoll 1991). An alternative is that late Precambrian atmospheric oxygen levels were already high (see discussion in McMenamin & McMenamin 1990), and that the later Precambrian radiation was caused by environmental changes which upset the biological balance of the period. The sharp negative carbon isotope excursion observed in Oman may be evidence of such an environmental change. That the fossil record is occasionally punctuated by rapid extinction of some groups of organisms and the rise of others (Eldridge & Gould 1972; Gould & Eldridge 1977) suggests that environmental changes, recorded by the carbon isotopes, may have triggered the evolution of new organisms seen thereafter in the latest Precambrian.

Acknowledgements

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