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SCIENTIFIC COMMENT

δ^{18}O values of mudrocks: More evidence for an ^{18}O-buffered ocean

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Abstract—The whole-rock δ^{18}O of mudrocks, as well as the δ^{18}O of the clay-sized silicate fraction, does not change in any systematic manner over Paleozoic and late Proterozoic time. Therefore, the δ^{18}O of the ocean has not changed (except a per mil or so as the result of glaciation/deglaciation) over the last billion years of Earth history.

1. INTRODUCTION

A quantitative understanding of the evolution of Earth's lithosphere-hydrosphere-atmosphere is a primary goal of the geological sciences. Sedimentary rocks provide an important record of Earth evolution, and various isotopic systems are proving to be very informative in unraveling the complexities of Earth's evolutionary history. Variations in oceanic ^{87}Sr/^{86}Sr and δ^{13}C as documented by carbonate rocks throughout Phanerozoic and late Proterozoic time demonstrate that not only have secular changes taken place, but that the isotopic records contain a wealth of information, the details of which we are only beginning to understand. Other isotopic systems show similar promise but are less well known (e.g., ϵNd, δ^{34}S, δ^{18}O–SO$_4$), in part because data are more difficult to obtain, or because they are impossible to obtain due to the absence of a rock record (as in primary anhydrite, for example). Quantitative determination of ancient paleotemperatures was the reason light stable isotope geochemistry was developed (Urey, 1947), and possible secular variation in the δ^{18}O of the world ocean has evoked considerable controversy ever since the earliest sediment analyses were accomplished.

There is no doubt that most kinds of sedimentary rocks become progressively depleted in ^{18}O back through geologic time (Veizer and Hoefs, 1976; Perry, 1967). Three explanations for this observation have engendered support: (1) The ancient oceans may have been depleted in ^{18}O relative to the modern ocean (Perry, 1967); (2) Earth temperatures may have been warmer in the past (Knauth and Epstein, 1976); or (3) Old sedimentary rocks may just have been subject to progressive alteration with time and burial (Degens and Epstein, 1962). The most voluminous data on sedimentary rocks have been derived from carbonates (Fig. 1), which, unfortunately, are more susceptible to alteration than are sandstones or mudrocks. Experimental studies (e.g., Beck et al., 1992) predict extensive reaction between calcite and pore waters, given many millions of years at temperatures characteristic of burial. Therefore "resetting" (not necessarily re-equilibration) of δ^{18}O values is easily accomplished (Lynch and Land, 1996), and δ^{18}O values of calcite are much more easily modified as the result of long periods of burial than are other isotopic systems such as those involving ^{13}C or ^{87}Sr, in which water/rock ratios are considerably smaller than is true for oxygen (Land, 1980; Banner and Hanson, 1990).

Our understanding of how the δ^{18}O of ocean water is controlled has a history nearly as long as light stable isotope geochemistry itself. Silverman (1951) suggested that the ocean is depleted relative to the mantle (Earth's main oxygen reservoir) because continental weathering generates ^{18}O-enriched products (principally clay minerals), which leave the reservoir of water (the ocean) ^{18}O depleted relative to the mantle (or to a "primordial ocean"). On recognizing the importance of hydrothermal circulation through ocean ridge systems, water budgets as proposed by Li (1972) and Perry and Tan (1972) were refined (Muehlenbachs and Clayton, 1976; Holland, 1984), but the conclusion of Silverman (1951) still stands: because of the large fractionation involved, continental weathering is a potentially important process controlling the depletion of ^{18}O in the ocean relative to the mantle. The observed difference between the oceans and the mantle (approximately 6‰) can be reasonably satisfactorily explained by some existing budgets (Muehlenbachs, 1986) which rely solely on ocean floor processes to control the δ^{18}O of the ocean, but provide no mechanism to change the δ^{18}O of the ocean because low-temperature and high-temperature sea floor processes are presumably coupled. Because of the long residence time of water in the ocean relative to hydrothermal circulation (10^7 years, Wolery and Sleep, 1988), and slow rates of chemical weathering on the continents, the δ^{18}O of the ocean is thought to be capable of only very slow changes (Holland, 1984; Gregory, 1991).

If continental weathering is a potentially important control on the δ^{18}O of ocean water, and since the position of the meteoric water line, which describes the oxygen isotopic composition of rain, is pinned to the isotopic composition of the ocean at any given time (Craig and Gordon, 1965), then the δ^{18}O of weathering products must reflect the δ^{18}O of the world ocean. If the ocean became depleted in ^{18}O by some mechanism, then rain would be similarly depleted, and so would clay minerals. Because the deposition of clay

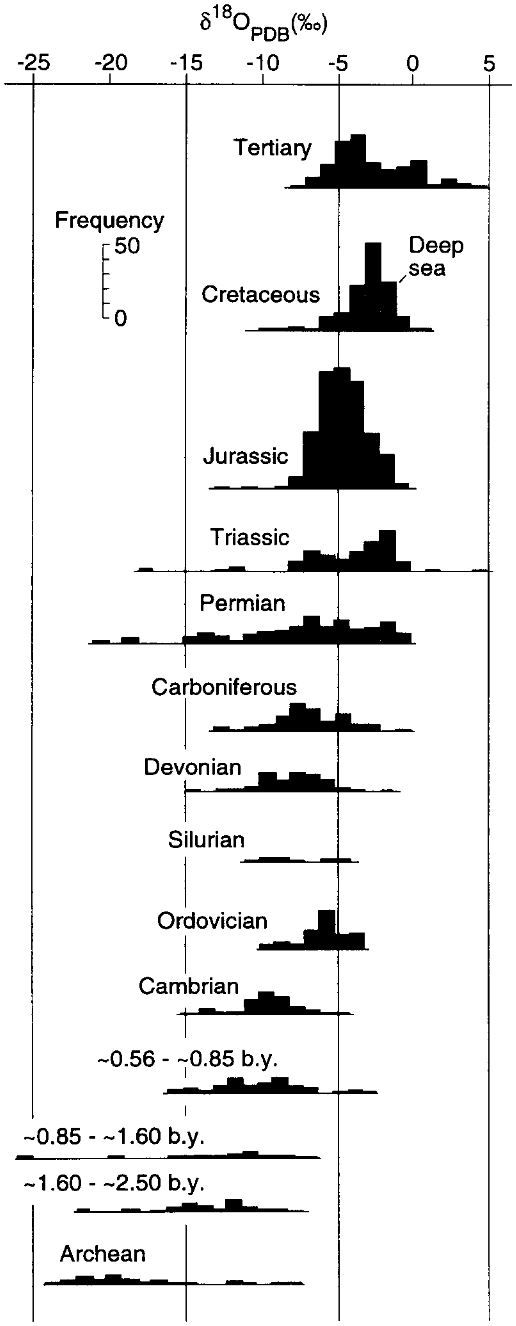

FIG. 1. $\delta^{18}O$ of carbonate rocks as a function of geologic time. Modified from Veizer and Hoefs (1976).

minerals is concentrated in the most common kind of sedimentary rock, mudrock, or shale, the $\delta^{18}O$ of shale should also ultimately reflect the $\delta^{18}O$ of the world ocean, assuming that the mix of "juvenile" and other kinds of rocks being weathered has remained the same.

It is unquestionably true, of course, that the clay minerals which constitute any given shale no longer have the $\delta^{18}O$ of the minerals that were deposited as mud. The clay minerals which are found in soils are believed to accurately record the $\delta^{18}O$ of the water and temperature at the time of formation (Lawrence and Taylor, 1972), although the clay-sized fraction of soils almost always contains unaltered phyllosilicates as well. Following deposition, and especially during burial, clay mineral assemblages derived from mechanical and chemical weathering are completely altered. Smectite, "discrete illite," and kaolinite are progressively destroyed, and authigenic illite and chlorite form, and then themselves recrystallize. Clay mineral diagenesis is well known to be sufficiently profound that primary $\delta^{18}O$ values of detrital phyllosilicates are completely destroyed.

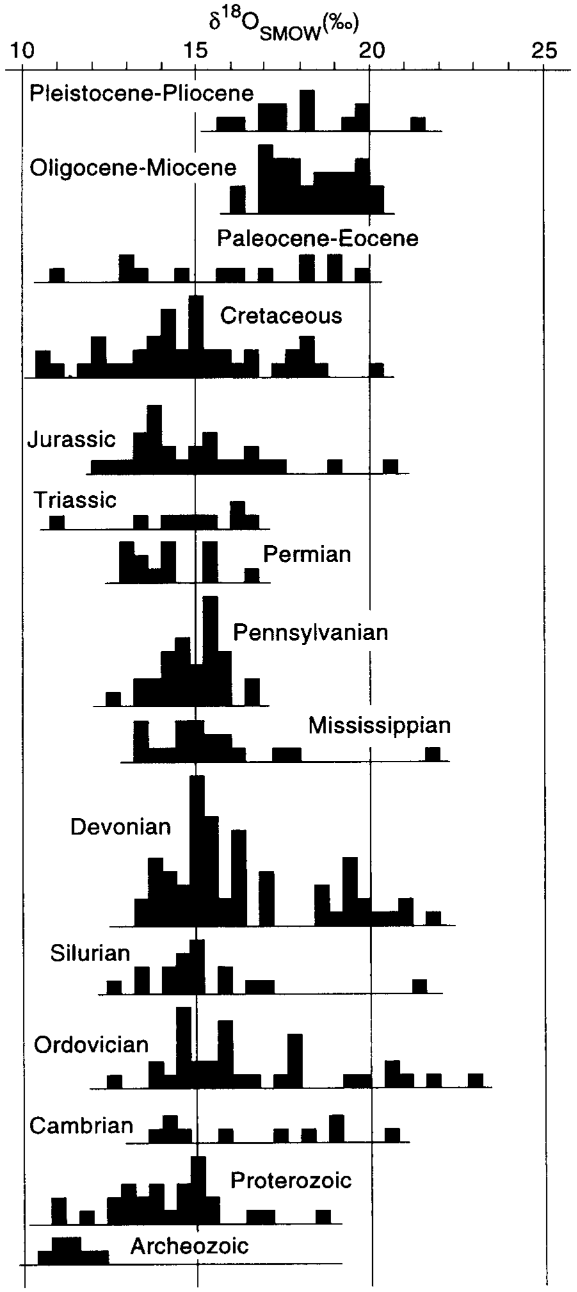

FIG. 2. $\delta^{18}O$ of carbonate-free mudrocks as a function of geologic time. Data from Table 1 and the references indicated with an asterisk.

TABLE 1. Mineralogy and oxygen isotopic composition of selected mudrocks. The percentages of I/S (mixed-layer illite/smectite), chlorite, and kaolinite, as well as the $\delta^{18}O$ value for clay, refer to the <2 μm size fraction.

Sample	Age	% clay	% quartz	% feldspar	% carbonate	% I/S	% chlorite	% kaol.	$\delta^{18}O$ whole rock	$\delta^{18}O$ clay
Harz Mountains, Germany	Devonian	45	39	16	0	92	8	0	14.5	13.6
Olentang Fm., In.	Devonian	46	45	6	0	92	8	0	18.7	17.9
Caballos Novaculite, Ok.	Devonian	41	53	6	0	70	0	30	22.0	
Ohio Fm., Indiana	Devonian	30	62	4	0	58	3	39	19.2	18.0
Port Evans Fm., Pa.	Devonian	26	45	7	21	74	10	16	20.9	20.0
Missouri Mt. Shale, Ar.	Silurian	57	34	8	0	82	0	18	21.4	
Alstate Fm., Tx.	Ordovician	26	58	5	11	93	7	0	21.3	24.0
Martinsburg Fm., Pa.	Ordovician	42	48	10	0	87	13	0	15.9	16.7
Marathon Fm., Tx.	Ordovician	40	47	8	6	95	5	0	21.1	
Womble Shale, Ar.	Ordovician	36	47	5	12	72	24	0	17.4	17.1
Woods Hollow Fm., Tx.	Ordovician	69	31	0	0	78	3	19	15.8	20.8
Ft. Pena Fm., Tx.	Ordovician	32	56	1	10	72	3	24	23.5	23.7
Hickory Fm., Tx.	Cambrian	48	24	26	0	47	8	45	15.9	17.5
Lion Mt. Fm., Tx.	Cambrian	20	53	21	4	84	16	0	14.5	17.7
Huronian "greywacke", Wi.	Pre-Camb.	38	40	22	0	80	20	0	11.1	10.9
La Hood Fm., Mt.	Pre-Camb.	36	13	7	43	100	0	0	16.5	14.8
Hokatana Fm., Az.	Pre-Camb.	23	13	4	58	91	9	0	15.0	17.3
Gowganda Tillite	Pre-Camb.	22	28	48	1	32	68	0	10.9	8.9
Torrascan slate, Australia	Pre-Camb.	28	29	41	1	8	92	0	14.4	13.2
Witwatersrand, S. Africa	Pre-Camb.	46	43	11	0	22	78	0	5.0	3.9

But the following reasoning suggests that the $\delta^{18}O$ of marine mudrocks, either whole-rock silicate analyses, or preferably, just illite (or mixed-layer illite/smectite) can yield useful information. The degree of postdepositional diagenetic alteration that sedimentary rocks undergo is controlled by the $\delta^{18}O$ of the reacting water, and variations in the temperature and water/rock ratio that the rocks experience (e.g., Suchecki and Land, 1983). Most thick shales are deposited in marine environments with seawater as the interstitial fluid. Shales deposited in freshwater environments are relatively rare, and can commonly be identified. Burt (1993) found that presumed freshwater shales were only about 1.4‰ depleted in ^{18}O relative to marine shales, a difference smaller than the difference (about 6‰) between the $\delta^{18}O$ of the ocean and temperate/tropical rain, which is responsible for most chemical weathering (Meybeck, 1994). Thus, it is unlikely that variations in the environment of deposition, even if they went undetected, would mask any secular trend of more than a few per mil which might exist in a relatively large compilation of mudrock analyses. Mudrocks are notoriously impermeable, and therefore very high water/rock ratios during burial alteration are not common. Furthermore, a similar temperature range over which burial diagenetic reactions (principally illite/smectite to illite) take place, between about 80 to 120°C, has been documented by many studies (Dunoyer de Segonzac, 1970; Hower et al., 1976; Eberl, 1989). It is well established that the reaction of smectite + kaolinite to illite + chlorite is accomplished during burial diagenesis, and not at either surficial or metamorphic temperatures. Once illite/smectite reaches a composition of about 80% illite, further reaction seems to be less extensive until true metamorphism occurs. Although the stability of 80% illite is being questioned (Eberl, 1993; Land et al., 1996; Lynch, 1996), and reaction probably does continue during deeper burial, the very low water/rock ratios which prevail during late burial prevent large changes in whole-rock $\delta^{18}O$ values from occurring. Therefore, the generalization that the $\delta^{18}O$ of mudrocks is controlled by the initial isotopic composition of the sediment and the degree of alteration is sufficiently reasonable to warrant trying to use mudrocks as a proxy for the $\delta^{18}O$ of the ancient ocean. If rocks (or, preferably I/S) which exhibit similar degrees of alteration are compared, and are found to be similar in $\delta^{18}O$, then it is unlikely that the initial sediments (or the ocean which controlled their $\delta^{18}O$) had different oxygen isotopic compositions.

2. DATA

Figure 2 summarizes 340 analyses of carbonate-free whole-rock shales (data from Table 1 and from references identified with an asterisk). A few values less than 10‰ have not been plotted, as well as some heavier than 24‰. Most analyses of pelagic sediments have also been omitted because this lithology is not a component of the continental mudrock record. Although more data are desirable, especially from the lower-most and pre-Paleozoic, no significant trend in oxygen isotopic composition is evident in rocks of Proterozoic through Mesozoic age. The somewhat enriched $\delta^{18}O$ values for Cenozoic mudrocks reflect the metastable nature of mineral assemblages which still exist in most of these young rocks.

Although far fewer analyses of the fine fraction of shales are available, and comparisons are difficult because of nonstandardized laboratory procedures, a similar compilation (Fig. 3) yields a similar conclusion. There is no evidence for secular change in the $\delta^{18}O$ of either mudrocks or of the fine clay fraction (mostly I/S). Therefore, there is no evidence for secular change in the $\delta^{18}O$ of the world ocean, or in temperature, over approximately the last 2 billion years of Earth history.

3. DISCUSSION

If the $\delta^{18}O$ or temperature of the ocean has not changed, then sedimentary rocks like carbonates and chert must be-

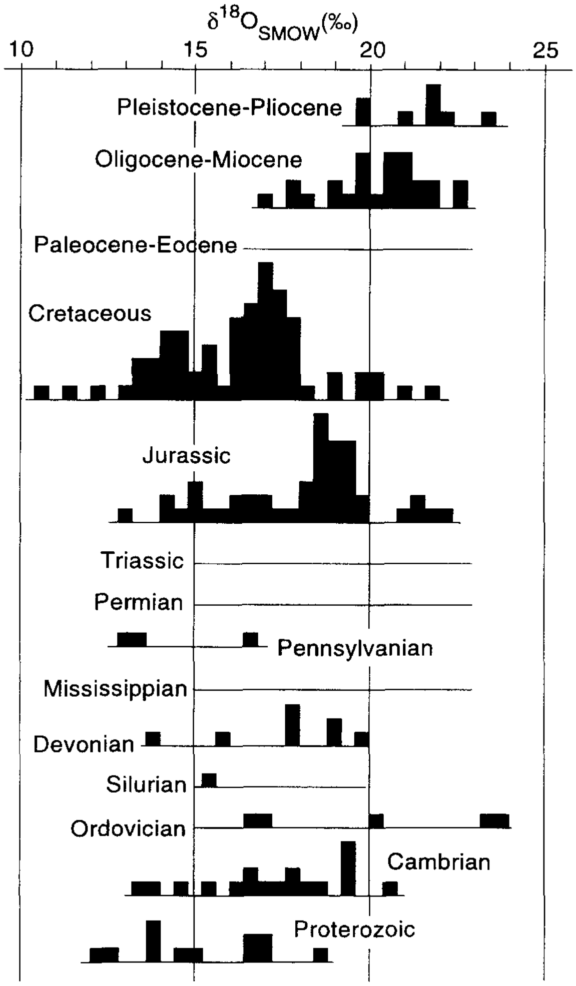

FIG. 3. $\delta^{18}O$ of the fine-fraction (mostly phyllosilicates) of mudrocks as a function of geologic time. Data from Table 1 and the references indicated with an asterisk.

come progressively ^{18}O depleted with time because of progressive diagenetic alteration, just as clay minerals are undoubtedly altered toward more depleted oxygen isotopic compositions with progressive burial. Mudrocks provide more useful information about ancient oceanic compositions than do chert or carbonate rocks because mudrock alteration is more predictable than is true of other kinds of lithologies due to lower and more uniform water/rock ratios at the time when the most profound stabilization reaction (of I/S to I) takes place.

Few authors have accepted higher Earth surface temperatures as a satisfactory explanation for ^{18}O-depleted Paleozoic rocks, and mudrocks do not support such a contention. Communities of marine organisms today become severely restricted at elevated temperatures, and it is difficult to envision long-term biochemical evolution at temperatures much higher than about 30°C (e.g., Schopf, 1980).

Progressive diagenetic alteration is therefore the preferred explanation for the ^{18}O-depleted nature of sedimentary rocks with geologic time. It is known that chert can recrystallize from an opal precursor to opal-CT (porcellanite), and then to microquartz chert (Berger and van Rad, 1972). In Paleozoic rocks, microquartz chert can exhibit long-term grain growth (Ostwald ripening?), either as the result of time and/or changes in porewater composition (Gao and Land, 1991), or as the result of an imposed thermal gradient (Jones and Knauth, 1979). Thus, there is no reason to believe that the $\delta^{18}O$ values of ancient granular microcrystalline quartz chert record any information whatsoever about the primary conditions of emplacement.

In the case of carbonates, we can be quite sure that the $\delta^{18}O$ of the ocean has not changed (except as the result of growth and demise of ice caps) since Pennsylvanian time. Microfauna from the deep sea clearly document an unchanging ocean back as far as the Cretaceous (Douglas and Savin, 1975), and studies of "unaltered" corals (Stanley and Swart, 1995) and careful studies of Pennsylvanian brachiopods (Grossman et al., 1993) provide evidence for an ^{18}O-invarient (±1‰) ocean back as far as the late Paleozoic. A growing body of data (Marshall and Middleton, 1990; Wadleigh and Veizer, 1992; Gao et al., 1996) is extending this conclusion back beyond early Paleozoic carbonate rocks as well.

When the secular trend in $\delta^{18}O$ of limestones is examined (Fig. 1), it is quite clear that these (mostly whole-rock) data suggest ^{18}O depletion of Mesozoic and Late Paleozoic rocks, a conclusion in conflict with subsequent studies. If the ^{18}O depletion of limestones back as far as the Pennsylvanian, as documented by compilations such as Fig. 1, is unquestionably due to diagenesis, then inferences about the $\delta^{18}O$ of the ocean prior to the Pennsylvanian are equally likely the result of progressive diagenesis, primarily as the result of compaction (stylolitization) in burial settings. Large (4‰), rapid excursions in oceanic $\delta^{18}O$, as proposed by Lohman and Walker (1989), are precluded.

There is also no doubt that a long-term, complex recrystallization history of dolomite accounts for the ^{18}O depletion of that mineral with increased age (Land, 1980; Gao, 1990; Malone et al., 1994), meaning that dolomite contains no useful information about the $\delta^{18}O$ or temperature of the ancient ocean.

4. CONCLUSIONS

Mudrocks, as well as ophiolites (Gregory, 1991), phosphates (Kolodny and Luz, 1991), and fluid inclusions in salt (Knauth and Roberts, 1991) do not change in $\delta^{18}O$ with geologic time, back as far as the early Paleozoic. Therefore, it is unlikely that the $\delta^{18}O$ of the world ocean could have changed more than about ±1‰ (except as a result of glaciation) during this time interval. ^{18}O depletion of sedimentary rocks with increasing age is the result of diagenesis, as porosity, small crystals, and subtle metastable domains in crystals are eliminated over the immense amounts of time available for reactions to proceed, especially at the elevated temperatures and pressures characteristic of burial.

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