Fossil Echinoderms As Monitor of the Mg/Ca Ratio of Phanerozoic Oceans

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Opinion has long been divided as to whether the Mg/Ca ratio of seawater remained constant during the Phanerozoic or underwent substantial secular change. Existing empirical evidence for the Mg/Ca of ancient seawater provides a poorly resolved and often controversial signal. Echinoderm fossils that have retained their bulk original chemistry, despite micrometer-scale changes, preserve a record of seawater Mg/Ca and confirm that major changes in Mg/Ca occurred during the Phanerozoic. Echinoderms from the Cambrian and from the Carboniferous to the Triassic indicate a seawater Mg/Ca of $\sim$3.3, whereas echinoderms from the Jurassic to the Cretaceous indicate a Mg/Ca of $\sim$1.4. The present seawater Mg/Ca is $\sim$5.

The major element composition of the ocean is controlled by the balance between input and output of seawater solutes (*1*, *2*). Two decades ago, the major ionic composition of the oceans was thought to have been constant for the past 500 million years (*1*), but, more recently, major oscillations in seawater chemistry have been proposed (*3*, *4*). The Mg/Ca ratio of seawater today is $\sim$5.2 mol/mol (*5*) and is controlled by the supply of these elements to the oceans by rivers by their exchange in hydrothermal flows at midocean spreading centers, and by their removal due to carbonate and evaporite precipitation. Estimated changes in these fluxes during the Phanerozoic have been used to model Mg/Ca seawater values and imply that this value has oscillated between 1.0 and 5.0 (*3*, *4*). This pattern has been correlated with changes in atmospheric CO_2 concentration, sea level, "icehouse" versus "greenhouse" conditions, and other first-order global cycles (*6*, *7*). The particular pattern of Mg/Ca modeled, however, depends on the values assigned to the fluxes, and these have been questioned (*8*, *9*). What is needed is a reliable archive of ancient seawater Mg/Ca values.

Evaporite minerals and fluid inclusions in evaporites (particularly halite) have been used to reconstruct seawater Mg/Ca (*4*, *10*). The deviation of fluid inclusion Mg/Cl data from the path calculated for closed-system evaporation of modern seawater is interpreted as being due to different initial compositions of seawater (*10*). Despite reservations on the use of a closed-system model (*9*) and the fact that deviations from this model are uniquely tied to compositional differences of the initial seawater, fluid inclusion data can be matched to Phanerozoic seawater Mg/Ca models (*10*).

The relative abundance of limestone and dolomite deposits has been proposed to reflect seawater Mg/Ca (*3*), with dolomite [$CaMg(CO_3)_2$] being more abundant at times of proposed low seawater Mg/Ca (*11*). The relative abundance of these rocks, however, is difficult to quantify; some suggest that the mass ratio varied cyclically during the Phanerozoic and correlated with sea level (*12*), whereas others claim its pattern is stepped, with a reduction in dolomite abundance $\sim$150 million years ago (*13*).

Similarly, the relative abundance of the dominant abiotic carbonate phase, calcite or aragonite, has been proposed as an indicator of seawater Mg/Ca (*4*, *8*, *14*). Today, shallow-water marine abiotic precipitation of carbonate occurs primarily as aragonite and Mg calcite. However, it has been proposed that, at certain times in the past, calcite (low-Mg calcite) was the dominant phase and that the alternation between aragonite and calcite seas correlates with variations in seawater Mg/Ca (*4*, *8*, *14*). Although experimental evidence support seawater Mg/Ca as a control on carbonate mineralogy, it is clear that many other interacting factors are involved, such as temperature, concentration of SO_4, saturation state and therefore atmospheric CO_2 (controversial), phosphate, and perhaps others (*15*–*18*).

Here, I suggest that fossil echinoderms can be used as a reliable monitor of seawater Mg/Ca. Modern echinoderms produce skeletons that have a large range in Mg content [5 to 19 mole percent (mol%) $MgCO_3$]. This variation is principally controlled by temperature (Fig. 1) (*19*–*30*). The Mg content of different skeletal units from a single skeleton and between different genera varies considerably. This variation is controlled physiologically (*31*) and causes the low r^2 value shown in Fig. 1. Echinoderm spines have less Mg content than robust skeletal plates (*32*) and are excluded from this study. Modern abiotic marine Mg-calcite cements have a range of Mg content similar to echinoderms and also vary exponentially with temperature (Fig. 1). The close correspondence between these two sets of data (Fig. 1) suggests that generally echinoderm biomineralization involves little discrimination against Mg, as opposed to biomineralization in other calcite-secreting organisms such as foraminifera.

All fossil echinoderm skeletons have undergone diagenetic change, but this can vary from minor modification of trapped organic matter to wholesale textural and chemical reorganization of the stereome. A total of 103 samples containing externally well-preserved ossicles were selected for study; 75 of these were rejected because severe diagenetic changes were identified with the use of the scanning electron microscope in backscatter mode. The remaining 28 all contain ossicles that retain original stereome microstructure (Fig. 2); some are composed of Mg calcite and in some the Mg calcite has been transformed to calcite and dolomite. The ossicles composed of calcite with micrometer-sized blebs of dolomite preserve their overall primary Mg/Ca composition (*33*–*35*).

The Mg composition of individual ossicles was taken as the mean of $\sim$10 individual microprobe spot analyses (*36*). Each spot

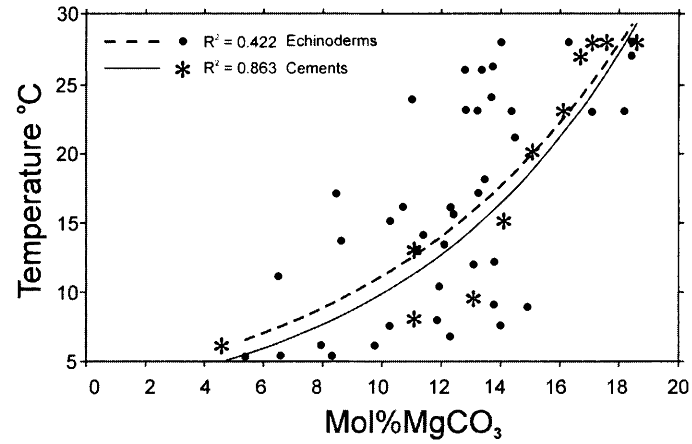

Fig. 1. Scatter diagram of mol% $MgCO_3$ versus temperature for modern echinoderms and marine Mg-calcite cements. Temperature was measured at collection sites (*19*–*30*). There is a close correspondence between exponential trend lines.

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was ~8 μm in diameter, and calcite/dolomite mixtures were averaged. Consistent results between spots are indicated by % standard deviations less than ~10%. The total variation in mol% $MgCO_3$ between 63 ossicles from the 28 well-preserved samples is from 3.3 to 12.5%. A maximum of seven ossicles were analyzed from one sample with a range of 1.5 mol% $MgCO_3$; the largest intrasample variation is 2.4% between three ossicles, but only single-ossicle analyses were completed on some samples. Modern tropical echinoids (*31*) have an average mol% $MgCO_3 = 16.3\%$ ($n = 61$, where n is the number of ossicles), with a range of 7.4% (Fig. 1). Intrasample variation requires further investigation.

The experimental determination of Mg partitioning in synthetic calcite has been extensively studied, and a range of coefficients for precipitation at 25°C (0.01 to 0.05) has been determined (*37*). This range is caused by a number of kinetic factors, some of which are difficult to quantify. Coefficients determined from seawater precipitation of synthetic material underestimate Mg found in marine Mg-calcite cements (*17*, *38*). Consequently, an effective partition coefficient for Mg in echinoderms is used here ($D^cMg = 0.03757$), calculated from (i) a mean $MgCO_3$ content of 16.3 mol% from modern tropical echinoids, (ii) a seawater composition of Ca = 411 parts per million (ppm) (10.2 mmol/kg) and Mg = 1290 ppm (53.0 mmol/kg), and (iii) a temperature of 25°C. To minimize the effects of temperature, echinoderm samples were selected from paleotropical or paleosubtropical regions. A reasonable temperature range for these regions at present is 20 to 30°C; during greenhouse epochs, maximum temperatures were probably higher (*39*).

The Mg/Ca of past seawater is calculated from mol% $MgCO_3$ of fossil echinoderms with the use of a single partition coefficient. For simplicity, no account is taken of temperature and other secular changes that will modify the D^cMg value, because the magnitude of these changes is uncertain and the effects of some kinetic factors are not yet understood. It is estimated that ignoring these factors may introduce a maximum error ~0.4 to the Mg/Ca values for seawater. The Phanerozoic range and pattern of Mg/Ca seawater variation match, in a general way, those predicted by existing mass balance models (*3*, *4*) and by Mg/Ca estimates from fluid inclusions in halite (*10*) (Fig. 3). Excluding the Cambrian data, there is an excellent match between the fluid inclusion and echinoderm data for seawater Mg/Ca. The presence of abundant aragonite cement in the early Cambrian (*40*) tends to support the higher Mg/Ca indicated by the echinoderm value. The Mg/Ca models of Wilkinson and Algeo and Hardie have substantial differences (Fig. 3) due to the former incorporating the effects of dolomitization and the latter ignoring them. The Mg/Ca values calculated from echinoderms are close to parts of the two model curves at different times (Fig. 3), and their overall concentration is similar, except for the Cambrian values. Echinoderms formed in seawater in the early Cambrian have Mg/Ca = 3.3 ($\sigma = 0.1$. $n = 3$); in the late Carboniferous, 3.4 ($\sigma = 0.2$; $n = 10$); and the late Triassic, 3.1 ($n = 1$). Mg/Ca values calculated for early Carboniferous seawater are substantially lower at 2.2 ($\sigma = 0.7$; $n = 19$); in the Jurassic, 1.4 ($\sigma = 0.2$; $n = 18$); and in the Cretaceous, 1.4 ($\sigma = 0.5$, $n = 4$), more than a factor of two lower than modern echinoderms.

Echinoderms to date have been ignored as a Mg/Ca seawater monitor. The data presented here are encouraging, but further analyses of existing samples and of many previously unstudied well-preserved echinoderms are required to substantiate the pattern of seawater Mg/Ca secular variation.

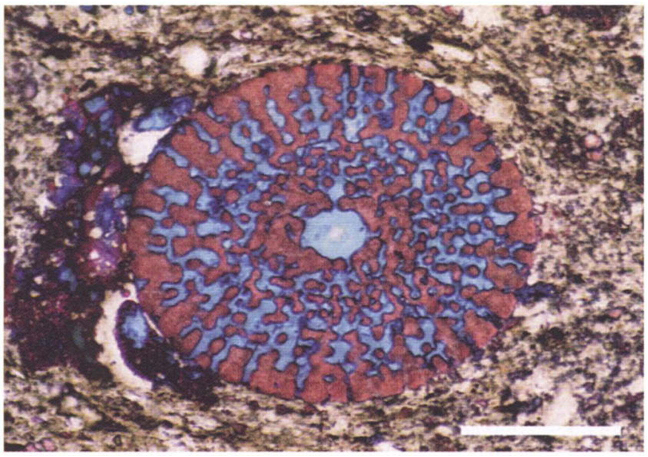

Fig. 2. A micrograph of a stained (*32*) thin section of crinoid ossicle set in silty clay from the Holder Formation (late Pennsylvanian), Dry Canyon, New Mexico. Crinoid skeleton (stereome) stains red and is composed of a mixture of calcite and dolomite (unresolved at this magnification) and is clearly differentiated from the cement that fills the ossicle's pores. The cement stains blue and is composed of ferroan calcite. Scale bar = 0.1 mm. The special preservation of this structure and retention of its original chemistry is due to the Mg-calcite skeleton changing to calcite and dolomite after its pores were filled by ferroan calcite cement. This cement acted as a crystal casket, confining transformation to internal reorganization of the skeleton (*34*).

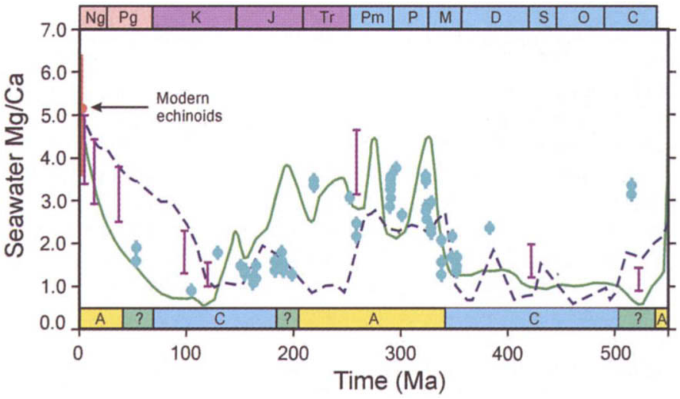

Fig. 3. Scatter diagram of seawater Mg/Ca against time. Mg concentration data for 28 fossil echinoderm samples recalculated as seawater Mg/Ca by using $D^cMg^{2+} = 0.03757$. Each blue dot represents an analysis of one ossicle (*36*) calculated at 25°C. Vertical blue lines represent possible temperature error from 13°C to 37°C on each blue spot. Mg concentration of modern tropical echinoids (*37*) converted to Mg/Ca with the use of $D^cMg^{2+} = 0.03757$ shown as orange spot, indicating the mean value ($n = 61$) = 5.1, and vertical line, indicating the range = 4.0 to 6.4. The dashed blue line is from the Wilkinson and Algeo Mg/Ca (*3*); the solid green line is from Hardie (*4*). The vertical purple lines are from fluid inclusion estimates (*10*). In the bottom bar, A represents aragonite sea and C, calcite sea, from Sandberg (*6*). Geological periods indicated in top bar: Palaeozoic era, pale blue; Mesozoic era, mauve; and Cenozoic era, pink. Geological periods indicated: Ng, Neogene; Pg, Paleocene; K, Cretaceous; J, Jurassic; Tr, Triassic; Pm, Permian; P, Pennsylvanian; M, Mississippian; D, Devonian; S, Silurian; O, Ordivician; and C, Cambrian.

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19. The sources of data for Fig. 1 are as follows: echinoderm data, composition, and temperature are from echinoid coronal plates from (*31*, *32*) and 24 crinoids from (*31*). Much chemical data exists for Mg-calcite cements, but few workers record temperature. The following have done so, and their data are used in Fig. 1 (*20–30*).
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41. Thanks are due to A. Smith, S. Marcus, E. Harper, N. Butterfield, A. Molineux, P. Jell, D. Erwin, and J. Wendt for providing specimens for this study and to S. De Villiers and S. Bishop for discussion. S. Reed assisted with the electron microprobe analysis.

Supporting Online Material
www.sciencemag.org/cgi/content/full/298/5596/1222/DC1
Materials and Methods

9 July 2002; accepted 9 October 2002

Spatial and Temporal Offsets Between Proxy Records in a Sediment Drift

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Chronologies for Late Quaternary marine sediment records are usually based on radiocarbon ages of planktonic foraminifera. Signals carried by other sedimentary components measured in parallel can provide complementary paleoclimate information. A key premise is that microfossils and other indicators within a given sediment horizon are of equal age. We show here that haptophyte-derived alkenones isolated from Bermuda Rise drift sediments are up to 7000 years older than coexisting planktonic foraminifera. This temporal offset, which is apparently due to lateral transport of alkenones on fine-grained particles from the Nova Scotian margin, markedly influences molecular estimates of sea surface temperatures. More broadly, the observation raises questions about both the temporal and the geographic fidelity of paleoenvironmental records encoded by readily transported components of sediments.

The development of multiple parallel proxy records derived from measurements of various sedimentary components is now commonplace for reconstruction of past changes in the ocean and climate. For example, the molecular sea surface temperature (SST) proxy $\mathrm{U}^{\mathrm{K}'}_{37}$ (*1–3*) complements information derived from the assemblages and oxygen isotopic (δ^{18}O) compositions of planktonic foraminifera (*4*). A requirement for the successful coupling of molecular and microfossil-based proxies is that they reflect water column conditions at the same time. Bioturbation can, however, mix particles with differing ages (*5*). Resuspension and lateral advection of fine particles, which lead to the formation of sediment drifts (*6*), mix vertically sinking (autochthonous) and horizontally drifting (allochthonous) particles, potentially inducing the same net effect. Where allochthonous inputs are substantial, paleoclimate proxies associated with fine particles can be chronologically and spatially decoupled from those associated with coarser particles (*7*). The problem is important because sediment drifts, in which a meter of depth may represent only 1000 years, are often targeted for studies of abrupt climate change (*8*, *9*).

Drift sediments on the Bermuda Rise have been investigated in detail (*7–11*). Prior radiocarbon data, as well as analyses of planktonic foraminifera (*Globigerinoides ruber*) conducted as part of this study, indicate deposition rates of 12 to 24 cm per thousand years (ky) during the past 1200 calendar years and $\sim$160 cm/ky from 17,000 to 23,000 calendar years before the present (yr B.P.) (Table 1) (cm/ky = cm per 1000 calendar years) (*8*, *10*, *12*). Table 1 also summarizes measured radiocarbon ages for total organic carbon (TOC), alkenones, and inorganic carbon in the fine fraction (FFIC) (particles $<$63 μm in diameter) from sediment intervals in three different cores (*13*). The first seven entries represent samples of Holocene age from a single box core. The average interval between samples is $\sim$200 years. The remaining entries represent sediments deposited during the late glacial and deglaciation, 16 to 24 thousand years ago. The temporal resolution in this series is significantly lower, with an average interval between samples of about 1300 years. In all samples, the radiocarbon ages of the alkenones, TOC, and fine carbonates significantly exceed those of the planktonic forams. For the alkenones, the average difference is 4200 ^{14}C years. The TOC and FFIC are on average $>$5000 ^{14}C years older than the forams.

The foram ages provide the most accurate indication of the age of each sediment horizon. Relative to other sedimentary components, forams are large ($>$150 μm) and dense. These sand-sized particles settle rapidly from the overlying surface waters (*14*). Although bioturbation can in some cases mix forams of different ages with one another (*5*), the high sediment accumulation rates at the Bermuda Rise minimize potential offsets due to this process (*15*). In support of this idea, measurements on another planktonic foram, *Globorotalia inflata* (*16*), from the same samples yielded ages that were identical, within uncertainties, to those of *G. ruber*. Finally, the presence of bomb ^{14}C in forams in the shallowest depth interval (Table 1) provides clear evidence of prompt deposition.

The above differences in radiocarbon age provide compelling evidence that a significant portion of the carbon in the alkenones, TOC, and fine carbonates is derived from some source other than surface waters overlying the

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