Geochimica et Cosmochimica Acta, Vol. 69, No. 4, pp. 953–961, 2005

0016-7037/05 $30.00 + .00

doi:10.1016/j.gca.2004.07.029

A critical evaluation of the boron isotope-*p*H proxy: The accuracy of ancient ocean *p*H estimates

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(*Received March* 5, 2004; *accepted in revised form July* 28, 2004)

Abstract—The boron isotope-*p*H technique is founded on a theoretical model of carbonate $\delta^{11}B$ variation with *p*H that assumes that the boron isotopic composition of carbonates mirrors the boron isotopic composition of borate in solution ($\delta^{11}B_{carb} = \delta^{11}B_{borate}$). Knowledge of the fractionation factor for isotope exchange between boric acid and borate in solution (α_{4-3}), the equilibrium constant for the dissociation of boric acid (pK^*_B), as well as the isotopic composition of boron in seawater ($\delta^{11}B_{sw}$) are required parameters of the model.

The available data suggests that both the value of α_{4-3} and the history of $\delta^{11}B_{sw}$ are poorly constrained. However, if one assumes that $\delta^{11}B_{carb} = \delta^{11}B_{borate}$, an empirical value for α_{4-3} can be estimated from the results of inorganic carbonate precipitation experiments. This exercise yields an α_{4-3} value of ~0.974 in accordance with recent theoretical estimates, but substantially deviates from the theoretical value of 0.981 often used to estimate paleo-ocean *p*H. Re-evaluation of ocean *p*H using an α_{4-3} value of 0.974 and published foraminiferal $\delta^{11}B$ values for the Cenozoic yield *p*H estimates that are relatively invariant, but unrealistically high (~8.4–8.6). Uncertainty increases as foraminiferal 'vital effects' are considered and different models for secular changes in seawater $\delta^{11}B$ are applied.

The inability to capture realistic ocean *p*H possibly reflects on our understanding of the isotopic relationship between carbonate and borate, as well as the mechanism of boron incorporation in carbonates. Given the current understanding of boron systematics, *p*H values estimated using this technique have considerable uncertainty, particularly when reconstructions exceed the residence time of boron in the ocean. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Establishing the long-term history of the partial pressure of atmospheric carbon dioxide (*p*CO_2) is a formidable challenge. Although qualitative paleo-*p*CO_2 representations are useful in establishing broad relationships between climate and greenhouse gas concentrations, quantification is necessary to understand the sensitivity of climate to changes in CO_2 concentration, how that sensitivity evolved over time, as well as to enhance our predictive skills for future climate change. Paleo-CO_2 concentrations older than those directly measured from ice cores have been estimated from model simulations (Berner and Kothavala, 2001), the carbon isotopic composition of organic and carbonate carbon (Arthur et al., 1988; Freeman and Hayes, 1992; Pagani et al., 1999), stomatal indices (Royer et al., 2001), carbon isotopic compositions of soil carbonates (Cerling, 1991) and goethites (Yapp, 2004), and the boron isotopic composition of marine carbonates (Sanyal et al., 1995; Pearson and Palmer, 2000). Each of these approaches has limitations and uncertainties specific to the assumptions underlying their methodology.

The potential relationship between the boron isotope composition of carbonates and ocean *p*H has wide appeal and, if reliable, could provide tremendous insight into the history of Earth's climate. In recent years the technique has been used to evaluate relative changes in Pleistocene ocean chemistry (Sanyal et al., 1995; 1997), as well as the evolution of ocean *p*H during the Cenozoic (Pearson and Palmer, 1999; 2000; Palmer et al., 1998). In this article we critically examine the assumptions underpinning the boron technique, as well as the accuracy of Cenozoic ocean *p*H trends reconstructed from foraminiferal $\delta^{11}B$ values for the past 60 million years.

2. THEORETICAL CONSIDERATIONS

2.1. The Relationship between Boron Isotope Composition and *p*H in Solution

Dissolved boron in seawater primarily includes mononuclear species $B(OH)_3$ (boric acid; planar, trigonally coordinated) and $B(OH)_4^-$ (borate; tetrahedrally coordinated). Polynuclear boron species are effectively absent at total boron concentrations in modern seawater (0.416 mmol kg^{-1} at $S = 35$; Miller, 1982) [e.g., Bryne and Kester, 1974] and are assumed to be inconsequential.

The dissociation of boric acid, given by the following equilibria:

$$B(OH)_3 + H_2O \Leftrightarrow H^+ + B(OH)_4^- \tag{1}$$

displays the importance of solution *p*H in determining the relative concentrations of the two aqueous boron species, where $B(OH)_4^-$ represents all borate species including ion pairs. If the apparent dissociation constant of boric acid ($K^*_{B\ (P,\ T,\ salinity)}$) is known then the distribution of each species in seawater as a function of *p*H (Fig. 1) is given by:

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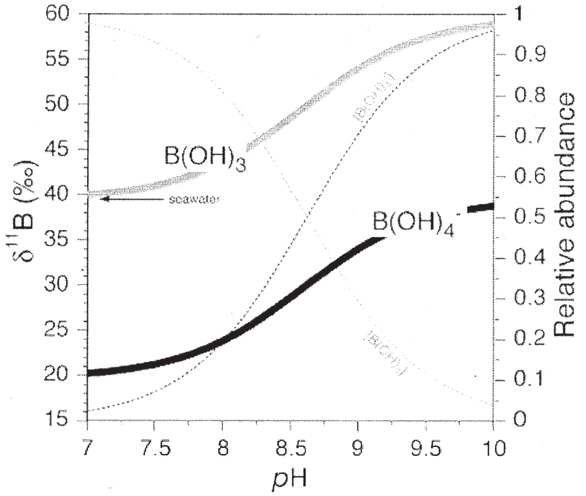

Fig. 1. Distribution of boric acid and borate in seawater and the theoretical relationship between the boron isotopic compositions of boric acid and borate and seawater pH established using the $p\mathrm{K}_{\mathrm{B}}^{*}$ of Dickson (1990), T = 25°C, and assuming $\alpha_{4-3} = 0.981$.

$$\log\left(\frac{[\mathrm{B(OH)}_4^-]}{[\mathrm{B(OH)}_3]}\right) = p\mathrm{H} - pK_B^{*} \tag{2}$$

where $pK_B^{*} = -\log(K_B^{*})$.

Equilibration between boron species in solution is rapid and characterized by an equilibrium isotopic fractionation resulting from differences in molecular geometries and vibrational energies of the trigonal and tetrahedral species (Urey, 1947). The equilibrium constant (${}^{10}_{11}K$) for the isotope exchange reaction

$$^{10}\mathrm{B(OH)}_3 + {}^{11}\mathrm{B(OH)}_4^- \Leftrightarrow {}^{11}\mathrm{B(OH)}_3 + {}^{10}\mathrm{B(OH)}_4^- \tag{3}$$

is greater than unity (Kakihana, 1977; Oi, 2000a), indicating B(OH)$_3$ is enriched in ^{11}B relative to B(OH)$_4{}^-$. For this equilibrium, the isotopic fractionation factor, α_{4-3}, ${}^{10}_{11}K$, and isotopic ratios of each species are related:

$$\alpha_{4-3} = \frac{1}{{}^{10}_{11}K} = \frac{R_{\mathrm{B(OH)}_4^-}}{R_{\mathrm{B(OH)}_3}} \tag{4}$$

where α_{4-3} is less than unity, and R is the ^{11}B/^{10}B ratio of borate and boric acid.

Equation 2 and 4 with mass balance for each isotope in seawater (sw)

$$^{11}\mathrm{B}_{\mathrm{sw}} = {}^{11}\mathrm{B(OH)}_4^- + {}^{11}\mathrm{B(OH)}_3 \tag{5}$$

$$^{10}\mathrm{B}_{\mathrm{sw}} = {}^{10}\mathrm{B(OH)}_4^- + {}^{10}\mathrm{B(OH)}_3 \tag{6}$$

result in a system of equations that can be solved for the isotopic composition of B(OH)$_3$ and B(OH)$_4{}^-$ relative to that of the total for the solution (Fig. 1):

$$R_{B(OH)_4^-} = R_{SW}\left(\frac{1 + \alpha_{4-3}10^{pK_B^{*}-pH}}{1 + 10^{pK_B^{*}-pH}}\right) \tag{7}$$

where R_{sw} is the ^{11}B/^{10}B ratio of seawater, and the acid dissociation constant is for the ^{11}B isotope. Values of K_B^{*} have only been determined on natural compounds containing mixtures of boron isotopes. However, if we assume that pK_B^{*} represents the abundance-weighted linear sum of $p^{11}K_B^{*}$ and $p^{10}K_B^{*}$, then $p^{11}K_B^{*}$ is expected to differ from that of a natural abundance mixture by less than 0.0035 if α_{4-3} is no smaller than 0.96. This small difference is a result of ^{11}B being the major natural abundance isotope. Thus, this substitution does not produce a significant (measurable) change in the pH dependence of fractionation.

2.2. Possible Modes of Boron Incorporation in Carbonates

Reconstructions of ancient ocean pH are modeled from the boron isotopic composition of carbonates. Studies attempting to reconstruct ancient seawater pH assume that boron incorporation is an equilibrium process between bulk solution and carbonate. The technique further assumes that isotopic fractionation of boron in carbonates is the same as in a model system where fractionation is identical to the trigonal/tetrahedral fractionation that occurs in solution (Fig. 1). Equilibrium requires that sorption/desorption rates are fast relative to crystal growth. Further, the value of $\delta^{11}\mathrm{B}_{carb}$ will be determined by the proportion of solid phase tetrahedral and trigonal boron and their respective isotopic compositions. If solid phase boron is entirely tetrahedral, boron isotopic compositions of carbonate could be identical to dissolved aqueous borate and reflect solution pH as in Figure 1. Deviation from the $\delta^{11}\mathrm{B}_{\mathrm{borate}}$–solution pH curve under equilibrium conditions can occur for a variety of reasons: (1) isotopic fractionation between solid phase and solution may differ from those occurring between aqueous boron species resulting in an isotopic composition that is offset from the dissolved species; (2) equilibrium might be established between a chemically distinct 'pool', rather than bulk ambient solution and carbonate (Elderfield et al. 1996; Erez, 2003); (3) solid-phase boron could represent some combination of trigonal and tetrahedral species that change as a function of pH and/or other physical conditions; and finally (4) the theoretical $\delta^{11}\mathrm{B}_{borate}$–$p$H relationship shown in Figure 1 is incorrect.

Alternatively, it is possible that boron incorporation in carbonate is associated with a non-equilibrium isotope fractionation. This would occur if one boron species is preferentially and irreversibly incorporated as a result of fast carbonate growth rates compared to exchange rates (i.e., kinetic isotopic fractionation is associated with uptake). In this case, the boron isotopic composition of carbonate would reflect the isotopic composition of the dissolved boron species that is incorporated plus the associated kinetic fractionation. Further, the magnitude of kinetic fractionation could change under varying conditions.

3. THE COORDINATION OF CARBONATE BORON

The size of B(OH)$_3$ and B(OH)$_4^-$ are similar to CO$_3^{-2}$ and both could substitute in the carbonate lattice. Based on charge balance considerations, coupled substitution is necessary. B(OH)$_4^-$ substitution could be charge balanced by the coupled substitution of an alkali for Ca^{+2} while B(OH)$_3$ substitution would substitute for CO$_3^{-2}$ and Ca^{+2}. Alternatively, Hemming and Hanson (1992) suggest that boron exists as a Ca(HBO$_3$),

Table 1. Published boron data from modern carbonates.

Sample		[B] (ppm)	δ^{11}B range	Average δ^{11}B
Modern Corals				
Vengosh et al., 1991	aragonite	64 ± 11	26.7–31.9	29.3 ± 2 (n = 7)
Hemming and Hanson, 1992	aragonite	58 ± 6	23.0–24.7	24.0 ± 0.6 (n = 11)
Gaillardet and Allegre, 1995	aragonite	53 ± 4	23.5–27.0	25.1 ± 1.2 (n = 7)
Hemming et al., 1998	aragonite	51 ± 2	23.9–26.2	24.8 ± 0.7 (n = 16)
Planktonic Foraminifera				
Vengosh et al., 1991	calcite	15 ± 5	14.2–19.8	16.4 ± 2.4 (n = 5)
Sanyal et al., 1995	calcite		22.0–23.3	22.8 ± 0.5 (n = 5)
Sanyal et al., 1997	calcite		18.4	18.4 ± 0.3 (n = 1)
Benthic Foraminifera				
Vengosh et al., 1991	calcite		13.3, 20.3, 32.0	
Sanyal et al., 1995	calcite		20.5–21.4	20.7 ± 0.3 (n = 5)
Other carbonates				
Hemming and Hanson, 1992	calcite	45 ± 11	20.8–23.2	22.3 ± 0.9 (n = 6)
Hemming and Hanson, 1992	aragonite	31 ± 19	19.1–24.8	22.1 ± 1.8 (n = 9)

with HBO_3^{-2} substituting for CO_3^{-2}. However, the existence of HBO_3^{-2} is questionable (Bryne and Kester, 1973).

The coordination and source of boron in carbonates has been inferred and determined through various approaches. Vengosh et al. (1991) studied the boron isotopic character of various modern marine carbonates and concluded that the range of isotopic values (14.2 to 32.2‰) was consistent with co-precipitation of both boron species, with an affinity for the tetrahedral anion (Table 1). This view, espoused by Ichikuni and Kikuchi (1972), Kitano et al. (1978), and Oi et al. (1989), requires that $\delta^{11}B_{carb}$ reflects a two end-member mixing relationship for a given pH that is proportional to the fraction of each boron species in the solid phase. A similar study performed by Hemming and Hanson (1992), measured boron isotopic values of biogenic and nonbiogenic marine carbonates. Given the narrow isotopic range of their results (19.1–24.8‰) and the similarity of these values with the theoretical $\delta^{11}B_{\text{borate}}-p$H curve based on an α_{4-3} value of 0.981 (Table 1; Fig. 1), this work concluded that carbonate boron and its isotopic character mirror dissolved borate.

NMR studies indicate that boron in aragonite is nearly entirely tetrahedrally coordinated, whereas calcite crystals contain both trigonal and tetrahedral coordinations with a predominance (90%) of the trigonal form (Sen et al., 1994). Trigonal boron is consistent with the mechanism of boron incorporation proposed by Hemming and Hanson (1992) (i.e., the substitution of HBO_3^{-2} for CO_3^{-2}), but the presence of tetrahedrally coordinated boron is not (Sen et al., 1994). One possibility is that the boron isotopic composition of carbonate boron derives from a mixing relationship between tetrahedral and trigonal forms, and thus supporting the conclusions of Vengosh et al. (1991). However, Hemming et al. (1995) provide experimental evidence that boron isotopic signatures are nearly identical for aragonite, high-Mg calcite, and calcite precipitated under similar pH (~8.0). Although the range of pH in these experiments was limited, these results suggest that minimal isotopic fractionations occur during the structural transformation of tetrahedrally coordinated boron to the trigonal form during incorporation. This is surprising because secondary kinetic isotopic effects are likely associated with the rupture of the hydroxyl bond and subsequent change in bond orientation. As an explanation, Sen et al. (1994) proposed that any additional kinetic effects are masked because the entire pool of adsorbed boron undergoing structural alteration is incorporated, and thus no fractionation is expressed.

Boron concentrations in carbonates ($[B]_{carb}$) can also be used to infer the source of carbonate boron. The concentration of boron and other trace elements within a carbonate lattice formed in equilibrium with seawater is a function of the partition coefficient (D) defined as:

$$D = \frac{(m_t/m_c)_s}{(m_t/m_c)_l} \tag{8}$$

Where m_t and m_c stand for the molar concentration of the trace and major element (or molecule) respectively, and subscripts s and l define solid and liquid phases (McIntire, 1963). The distribution coefficient of many trace elements is also controlled by structural parameters of the solid phase, and thus varies between calcite, aragonite, and dolomite phases (Veizer, 1983). This relationship appears to be valid for boron incorporation as well (Kitano et al., 1978; Hemming et al., 1995; Hobbs and Reardon, 1999).

In general, co-precipitation of boron in carbonates follow a pattern of increasing $[B]_{carb}$ with increasing [B] in solution. Given the correspondence between $[B(OH)_4^-]$ and pH, it is anticipated that $[B]_{carb}$ will increase with increasing pH if the tetrahedral species is solely or predominantly adsorbed at the mineral surface. This expectation is largely satisfied by inorganic precipitation experiments (Sanyal et al., 2000; Hobbs and Reardon, 1999) and one foraminifera culture (Sanyal et al., 1996) (note: cultures performed on *Globerigerina sacculifer* (Sanyal et al., 2001) do not show expected patterns), however, changes in both the rate of calcite precipitation (Hemming et al., 1995; Hobbs and Reardon, 1999), mineral surface charge (Su and Suarez, 1995), and crystal growth mechanisms (Hobbs and Reardon, 1999) cannot be ruled out as important controls on boron incorporation in these experiments. Nevertheless, if equilibration with trigonally coordinated boron is an important influence on the total boron concentration in carbonates, higher δ^{11}B values under low pH conditions would be anticipated (that is, if the theoretical curve in Fig. 1 is correct and fractionations specific to boric acid adsorption do not occur). But this behavior is not observed, instead, higher $\delta^{11}B$ values are associated with both higher *p*H and $[B]_{carb}$ (Sanyal et al., 1996). Thus, despite uncertainties, the correspondence between $[B]_{carb}$ and $\delta^{11}B_{carb}$ is compelling and supports an important influence of $[B(OH)_4^-]$ during boron incorporation in the carbonate lattice.

4. PARAMETERS OF THE $\delta^{11}B_{carb}$-*p*H MODEL

Spivack et al. (1993) pioneered the application of foraminiferal $\delta^{11}B$ to assess ancient ocean *p*H. In this work, boron fractionation associated with boron adsorbed onto clay surfaces (Palmer et al., 1987) was used as an analog for water/carbonate fractionation ($\delta^{11}B = -72.6 + 5.93*pH$). Recent studies abandon this approach and generally assume that $\delta^{11}B$ of foraminiferal boron is identical to borate in solution, following a $\delta^{11}B$-*p*H relationship that is similar (Sanyal et al. 1995), or identical (Pearson and Palmer, 2000), to the theoretical curve expressed in Figure 1. Although the validity of this assumption remains in question, the accuracy of reconstructed *p*H values from this approach depends upon on the validity of the theoretical $\delta^{11}B$-*p*H curve, and thus the accuracy of pK_B^*, α_{4-3}, and the $\delta^{11}B$ of seawater values used in its construction (Eqn. 7).

4.1. The Apparent Dissociation Constant of Boric Acid (pK_B^*)

The dissociation of boric acid has been studied under a range of temperatures and solution media using various *p*H scales (i.e., NBS, "total" hydrogen scale) including freshwater, ionic solutions (Owen and King, 1943; Dyrssen and Hansson, 1973; Byrne and Kester, 1974; Hershey et al., 1986), and synthetic seawater (Hansson, 1973; Dickson, 1990; Roy et al., 1993). Pressure dependence has also been assessed (Culberson and Pytkowicz, 1968). In general, pK_B^* increases with decreasing temperature and salinity. Differences in published calibrations of pK_B^* are attributed to differences in ionic media and measurement techniques, as well as the *p*H scale applied. Further, estimation of pCO_2 from *p*H requires that the dissociation constants for carbon dioxide equilibria (i.e., K_H, K_1, and K_2) are determined on the same *p*H scale. In this regard, the "total" hydrogen scale has great appeal (Dickson, 1984).

Various calibrations of pK_B^* have been applied in boron isotope-*p*H studies. Sanyal et al. (1995) applied the results of Lyman (1956); Hemming and Hanson (1992) utilized the work of Hershey et al. (1986), and Palmer et al. (1998) applied pK_B^* values determined by Dickson (1990) using the "total" hydrogen scale. The work of Dickson (1990), confirmed by Roy et al. (1993), agrees with the results of Hansson (1973), and is currently considered the most accurate calibration of pK_B^* (Millero, 1995). Accordingly, we have applied the results of Dickson (1990) in all calculations for the present study.

4.2. The Equilibrium Isotope Fractionation Factor (α_{4-3})

Boron isotope-based *p*H is largely determined by the value of α_{4-3} used to construct the theoretical $\delta^{11}B$-*p*H curve. In this regard, the theoretical result of Kakihana et al. (1977) is commonly applied (Sanyal et al., 1995; Pearson and Palmer, 2000). Kakihana et al. (1977) calculated α_{4-3} on the basis of reduced partition functions using the Wilson's GF-matrix method and found α_{4-3} to be relatively insensitive to temperature between 0°– 60°C. A value of 0.981 calculated at 25°C predicts a maximum fractionation of ~19‰ at low *p*H between aqueous solution (i.e., total [B]) and carbonates when the majority of aqueous boron is trigonally coordinated (Fig. 1). However, some carbonate studies appear to violate this isotopic limit [i.e., Vengosh et al., 1991; Spivack and You, 1997).

Recently, Oi (2000a) calculated α_{4-3} on the basis of reduced partition function ratios (RPFR) determined from various molecular orbital (MO) theories including the Hartree-Fock self-consistent field method (HF), Møller-Plesset perturbation theory, and the density functional theory. At 25°C, a range of α_{4-3} values can be calculated depending on the MO theory applied. Oi (2000a) concludes that the HF theory in combination with the 6–31G(d) basis set, the combination most commonly used in MO calculations, is the most appropriate given that more advanced MO theories failed to produce better results and subsequently used this theory to calculate RPFR of polyboric acids and polyborate anions (Oi, 2000b). This approach yields an $\alpha_{4-3} = 0.975$.

Theoretical isotope fractionation factors require experimental support, however, few experiments specific to the carbonate system have been performed. Hemming et al. (1995) precipitated various inorganic carbonate phases at a *p*H of ~8 and determined an empirical separation factor between the fluid and the solid phase of 0.984. To date, Sanyal et al. (2000) performed the most robust inorganic precipitation experiment. Their results demonstrate that the $\delta^{11}B$ of inorganic calcite precipitated at a *p*H of 7.9, 8.3, and 8.6 increases with increasing *p*H. However, their data are clearly offset from the theoretical curve generated when an α_{4-3} of 0.981 is applied (Fig. 2). Two explanations are possible: the α_{4-3} used to construct the theoretical curve is correct and additional fractionations occur during boron incorporation in the carbonate lattice, or the value of α_{4-3} from the work of Kakihana et al. (1977) is incorrect.

The primary assumption of the boron isotope-*p*H proxy assumes that $\delta^{11}B_{carb} = \delta^{11}B_{borate}$. However, this assumption is uncertain because the relationship between of the $\delta^{11}B_{borate}$ and *p*H is based on a model generated from a *theoretical* value of α_{4-3}. As shown in Figure 2, the results of Sanyal et al. (2000) deviate from the slope of a theoretical curve constrained by the assumption that $\delta^{11}B_{carb} = \delta^{11}B_{borate}$, and thus potentially suggests the assumption is faulty. Nevertheless, if the relationship $\delta^{11}B_{carb} = \delta^{11}B_{borate}$ is assumed correct, then we can approximate an *empirical* value of α_{4-3} from the results of inorganic carbonate precipitation experiments performed by Sanyal et al. (2000). The 'best fit' curve yields an α_{4-3} value of ~0.974 (Fig. 2), which is similar to the theoretical results of Oi (2000a) using HF theory with the 6–31G(d) basis set. If the empirical α_{4-3} value is correct, its application in Eqn. 7 substantially alters the character of the $\delta^{11}B_{carb}$–*p*H relationship, and thus estimates of ocean *p*H derived from the model.

4.3. The Evolution of Seawater $\delta^{11}B$

The residence time of boron in the oceans has been estimated between 14 and 20 myr, (Taylor and McLennan, 1985; Spivack and Edmond, 1987; Lemarchand et al., 2000; 2002) and thus substantial fluctuations of $\delta^{11}B_{sw}$ are unlikely over periods shorter than a few millions of years. Long-term changes in

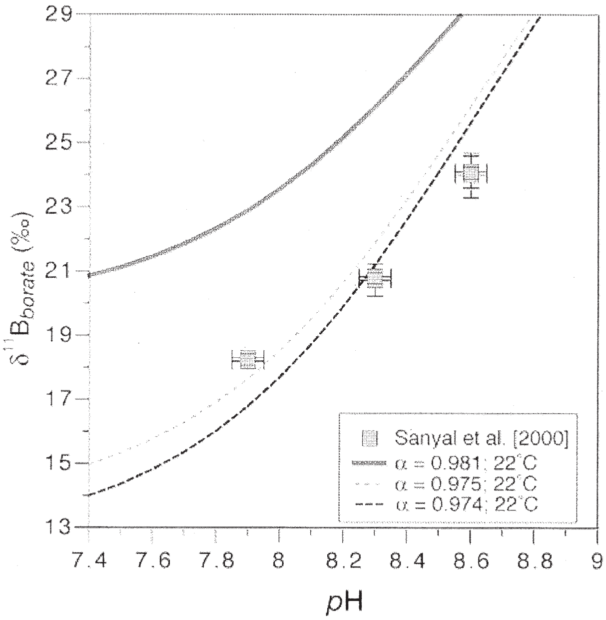

Fig. 2. Comparison of the theoretical δ^{11}B-pH relationship (α_{4-3} = 0.981, $p\mathrm{K}_\mathrm{B}^*$ of Dickson (1990), T = 22°C) with the results of inorganic carbonate precipitation experiments of Sanyal et al. (2000). Dashed lines represent values for α_{4-3} that fit the experimental results assuming carbonate boron is isotopically identical to borate in solution. Note: the results of Sanyal et al. (2000) were explicitly recalculated from published results using the following relationships: $\alpha_{(\mathrm{A}\text{-}\mathrm{B})} = \delta_\mathrm{A} + 1000/\ \delta_\mathrm{B} + 1000$; $\varepsilon_{(\mathrm{A}\text{-}\mathrm{B})} = 1000\ln\ \alpha_{(\mathrm{A}\text{-}\mathrm{B})}$; $\varepsilon_{(\mathrm{A}\text{-}\mathrm{B})} = (\delta_\mathrm{A} - \delta_\mathrm{B})/(1 + \delta_\mathrm{B}/1000)$.

$\delta^{11}B_{sw}$ have been reconstructed in various ways. Spivack et al. (1993) constrained $\delta^{11}B_{sw}$ by analyzing both the B concentration ([B]) and δ^{11}B value of pore fluids from a single core characterized by >99% carbonates. While [B] and δ^{11}B values of the pore fluids remained essentially constant through the depth of the core (~21 myr), it is important to note that the behavior of boron is rather non-conservative and that multiple reaction mechanisms involve boron during sediment burial (Brumsack and Zuleger, 1992; You et al., 1995; Spivack and You, 1997; Williams et al., 2001). These observations raise concerns regarding the accuracy of temporal $\delta^{11}B_{sw}$ records from pore fluid analysis.

Pearson and Palmer (2000) estimated paleo-$\delta^{11}B_{sw}$ for discreet time intervals by calculating pH-depth profiles from δ^{11}B values of depth-stratified foraminiferal using a range of $\delta^{11}B_{sw}$ values. Given Eqn. 7, a foraminiferal δ^{11}B value will yield a specific pH value for a given value of $\delta^{11}B_{sw}$. Thus, a pH-depth profile can be constructed from a number of foraminifera species with known, or inferred calcification depths, while the value of $\delta^{11}B_{sw}$ that is used in the calculation of pH adjusts the character of the pH-depth profile (Fig. 3a). Pearson and Palmer (2000) appropriately assumed limitations in the range of pH variation with depth, and selected a value for $\delta^{11}B_{sw}$ when ancient pH-depth profiles matched modern patterns. Confidence in the value of $\delta^{11}B_{sw}$ determined by this approach can be characterized by the uncertainty of the slope of pH decrease with depth (Fig. 3b). Uncertainty in pH-depth slope derives from the difficulty in assigning a narrow range of calcifying depths to individual foraminiferal species, species-dependent isotope effects, the analytical uncertainty of the carbonate δ^{11}B value, as well as the accuracy and/or veracity of the $\delta^{11}B_{carb}$-pH technique itself. If consideration is restricted to the precision of inferred depths of foraminifera, as well as the analytical error of δ^{11}B measurements, the resulting uncertainty spans the entire range of possible $\delta^{11}B_{sw}$ and thus reflects on the accuracy of $\delta^{11}B_{sw}$ determined by this approach.

Compared to the results of Pearson and Palmer (2000), distinctly different temporal $\delta^{11}B_{sw}$ trends have been simulated

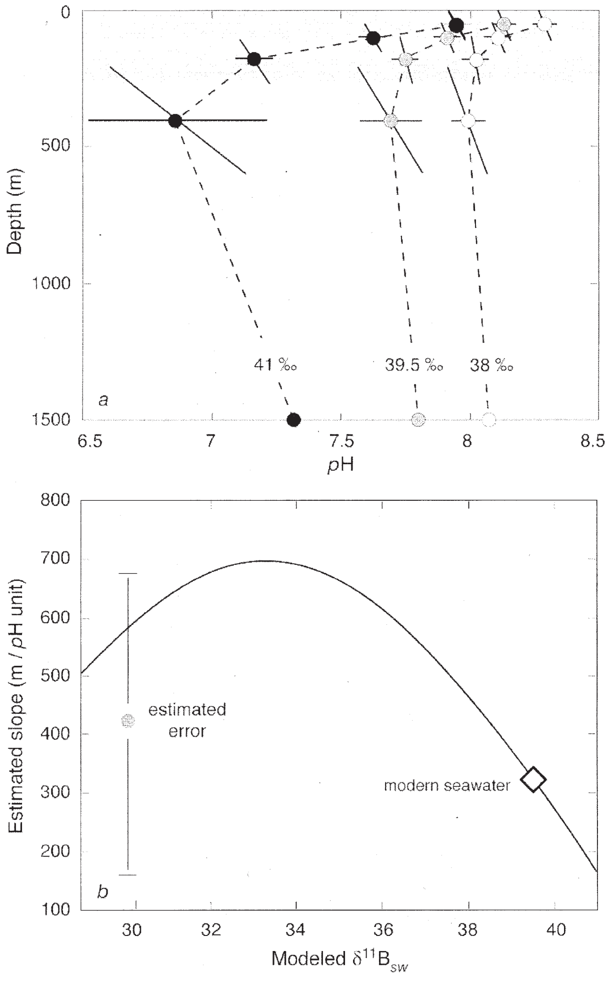

Fig. 3. Model for reconstructing ancient seawater δ^{11}B values based on the analyses of the pH-depth profiles (after Pearson and Palmer, 2000). (a) Effect of varying seawater δ^{11}B values on the shape of the calculated pH-depth profile. Data come from Pearson and Palmer (1999) and correspond to the analysis of a unique carbonate δ^{11}B profile obtained from foraminiferal species calcifying their test at different water depths. Open circles correspond to the pH values calculated for $\delta^{11}B_{sw}$ = 38‰; gray circles; $\delta^{11}B_{sw}$ = 39.5‰; and black circles; $\delta^{11}B_{sw}$ = 41‰. (b) Sensitivity test of the slope of estimated pH decline on the modeled marine δ^{11}B value. The slope is calculated using foraminiferal species living within the mixed layer (0–100 m) and within the thermocline (100–250 m) represented by the gray band in Figure 3a. These depth classes best define the slope of the pH decrease with depth by minimizing the interspecies overlaps in the calcification depths and avoiding the wide range of potential calcification depths for the deep-sea species. The error bar represents the uncertainty in estimating the pH profile shape attributed only to the data dispersion (i.e., calcification depths and carbonate δ^{11}B analyses). Other sources of error are not reported in this graph.

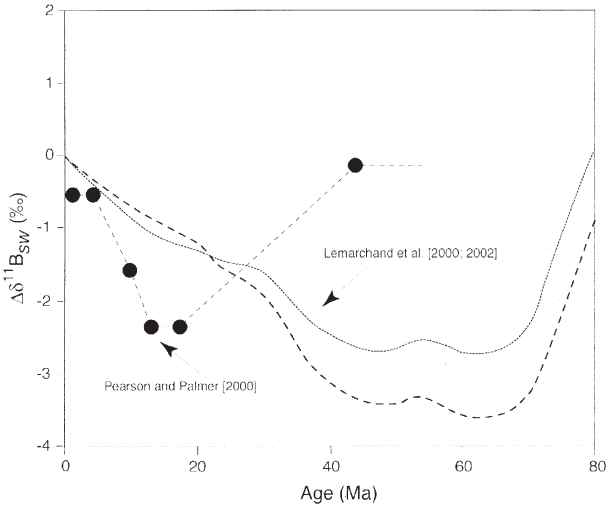

Fig. 4. Models of seawater $\delta^{11}B_{sw}$. Results are expressed as deviation from the modern value. Black circles: derived from *p*H-depth profile analyses (Pearson and Palmer, 2000), Dashed line: responses of boron oceanic budget models for two distinct scenarios of continental discharge. Dotted line; constant riverine input, dashed line; varying riverine discharge (Lemarchand et al., 2000; 2002).

from numerical models (Fig. 4) (Lemarchand et al., 2000; 2002). These studies propose that temporal fluctuations of $\delta^{11}B_{sw}$ are driven, at first order, by the balance of continental supply and uptake from seawater during the low temperature weathering of the oceanic crust. Because the flux of boron into and out of the oceans is not known for the past, each flux is assigned to other geological processes that are better understood. For example, boron co-precipitation in carbonate is proportional to total carbonate deposition, boron adsorption onto clays is a function of the suspended sediment supply by rivers and uptake by oceanic crust alteration, and hydrothermal inputs are assigned to estimates of sea-floor spreading rates. Modeling ancient $\delta^{11}B_{sw}$ assumes knowledge of the modern boron oceanic budget, however, some boron fluxes are still poorly constrained (Kopf and Deyhle, 2002). Further, how the continental boron flux and the mean riverine $\delta^{11}B$ value varied through time remains unconstrained, but critical in reconstructing $\delta^{11}B_{sw}$.

In summary, accurate knowledge of $\delta^{11}B_{sw}$ over long-time scales is lacking and thus currently represents a severe limitation in the application of the boron isotope-*p*H proxy.

5. VITAL EFFECTS AND DIAGENETIC CONSIDERATIONS

There is clear evidence for species-dependent "vital" effects on the boron isotopic composition of foraminiferal carbonates (Sanyal et al., 1996; Hönisch et al., 2003). Culture experiments performed on planktonic foraminifers *Orbulina universa* (Sanyal et al., 1996) and *Globerigerina sacculifer* (Sanyal et al., 2001) show isotopic offsets from each other and the $\delta^{11}B$-*p*H curves calculated using α_{4-3} values of 0.981 and 0.974 (Fig. 5). These isotopic differences are attributed to *p*H differences within the microenvironment or at the site of calcification for each organism (Sanyal et al., 2001; Erez, 2003). Microenvironment *p*H varies diurnally (Rink et al. 1998) and thus *p*H implied by foraminiferal $\delta^{11}B$ values from the natural environment likely represent an integrated signal dictated by specific growth conditions. Given the available evidence, biologic effects cannot be ignored.

Sanyal et al. (2001) suggest that once species-specific $\delta^{11}B$-*p*H relationships are established they can be used to correct offsets specific to coeval extinct species. However, Figure 5 indicates that the magnitude of these biologic offsets with respect to the theoretical or empirical curves varies with *p*H, making accurate corrections difficult. Differences between the slope of theoretical curves, empirical data, as well as changes in biologic offsets with *p*H, imply that one or more factors influence these relationships, including (1) the possibility that *p*H differences between seawater and calcifying microenvironments in foraminifera are not constant; (2) the value of pK_B^* applied is incorrect; and/or (3) the magnitude of boron isotopic fractionation during boron incorporation varies with *p*H.

Few data have been reported for boron content and isotopic compositions in ancient carbonates (Vengosh et al., 1991). The available data indicate the many ancient carbonates are characterized by low $[B]_{carb}$ and $\delta^{11}B_{carb}$ values (i.e., 1.5 to 8.4‰) compared to modern carbonates, suggesting postdepositional alterations impact $[B]_{carb}$ and lead to enrichment of ^{10}B (Spivack and You, 1997). Perhaps the best evidence that early diagenesis poses a serious limitation for boron isotope-based *p*H determinations is given by Gaillardet and Allègre (1995), for corals, and Spivack and You (1997) for bulk core-sample carbonate. In corals, boron isotopes appear to be affected by subtle diagenetic changes even for pure selected aragonitic phases (Gaillardet and Allegre, 1995) as indicated by an inverse $\delta^{11}B$ vs. 1/B correlation for Holocene corals. These results

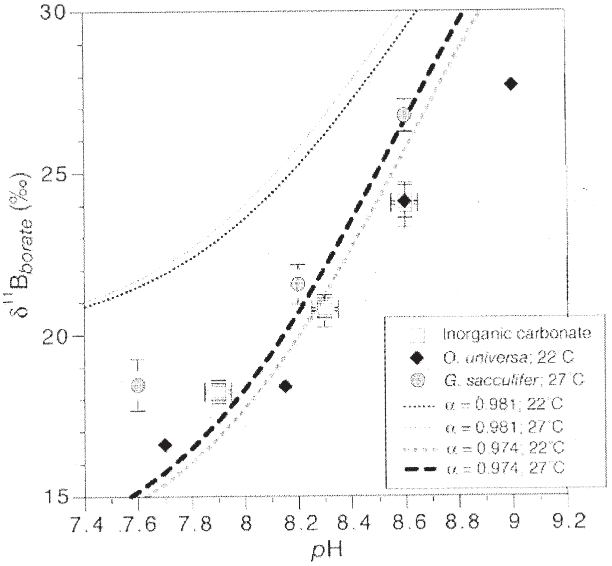

Fig. 5. Comparison of foraminifera cultures, inorganic carbonates, and theoretical curves. Shaded circles; *Globerigerina sacculifer* (Sanyal et al., 2001), closed diamonds; *Orbulina universa* (Sanyal et al., 1996), open squares; inorganic calcite (Sanyal et al., 2000). Note: the results of Sanyal et al. (2000; 2001) were explicitly recalculated from published results (see Fig. 2 caption).

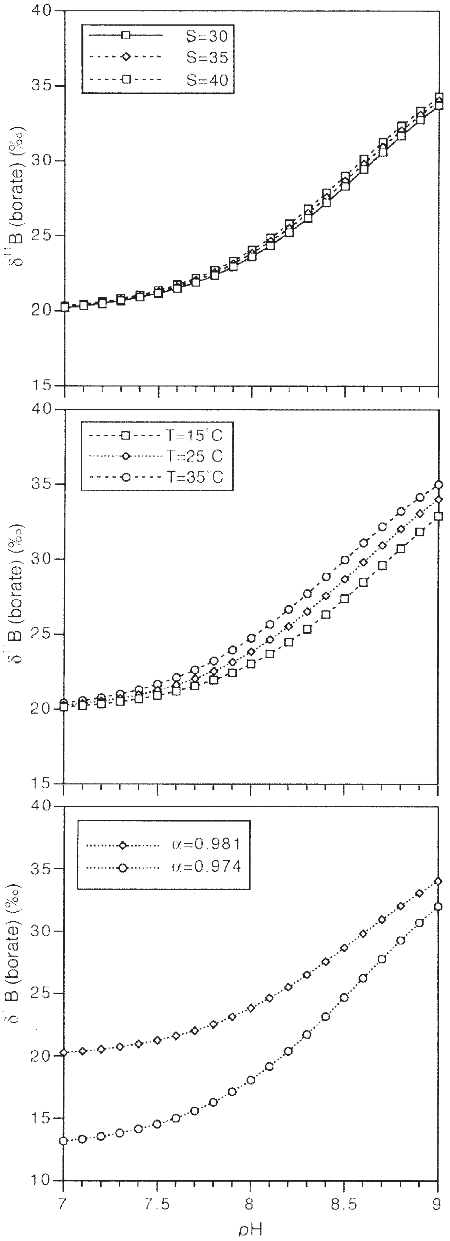

Fig. 6. The effect of (a) salinity and (b) temperature on pK_B^* and the resulting $\delta^{11}B_{borate}$-pH relationship ($\alpha_{4-3} = 0.981$, pK_B^* of Dickson, 1990). (c) The effect of different α_{4-3} values on $\delta^{11}B_{borate}$-pH relationship.

indicate that even pure aragonitic phases do not guarantee a primary boron signature.

The effect of dissolution was recently examined for species-specific planktonic foraminifera ranging in age from the Present to 5 Ma (Wara et al., 2003). This study noted a positive relationship of $\delta^{11}B$ values with average shell mass. $\delta^{11}B$ values appear to decrease with decreasing shell mass, suggesting that ^{10}B is preferentially removed during calcite dissolution. Furthermore, $\delta^{11}B$ values correlate well with Mg/Ca ratios. Given the relationship between Mg/Ca and calcification temperature (Rosenthal et al., 1997), this data suggests that temperature may be influencing the fractionation of boron during its incorporation into the calcite lattice.

6. DISCUSSION

Seawater pH values, derived from foraminiferal $\delta^{11}B$ values, have been used to estimate the Cenozoic history of pCO_2 (Spivack et al., 1993; Palmer et al., 1998; Pearson and Palmer, 1999; 2000). This approach demands that pH values are highly constrained as minor pH changes imply large atmospheric CO_2 fluctuations. For example, assuming the total dissolved inorganic carbon (DIC) in seawater remains constant, a 0.2 unit decrease in seawater pH corresponds to an atmospheric CO_2 concentration twice the present value. Limiting the uncertainty of estimated pH values within ± 0.2 requires that $\delta^{11}B_{sw}$ is known with a precision better than ± 1.5 ‰. In addition to the assumptions underlying the boron isotope-pH technique, calculation of pCO_2 from pH requires further consideration of alkalinity or DIC (Pearson and Palmer, 2000). Although assumptions pertinent to the history of ocean chemistry add additional layers of uncertainty on estimated pCO_2 (Caldeira and Berner, 1999; Sundquist, 1999), it is clear that the precision of pH values generated by the boron-isotope technique needs to be highly refined to accurately quantify long-term changes in pCO_2. Questions regarding the mode of boron incorporation, the precise nature of isotopic inheritance, and diagenesis aside, it remains important to understand the sensitivity of the $\delta^{11}B$-pH curve in relationship to the uncertainties and variables that affect it.

In general, errors in pH introduced by errors in temperature or salinity estimates are far outweighed by uncertainties surrounding the appropriate value for α_{4-3} and seawater $\delta^{11}B$ through time (Fig. 6). Cenozoic pH values of Pearson and Palmer (2000) are calculated using an α_{4-3} value of 0.981. However, given the previous discussion, a value of ~0.974 appears more appropriate for carbonates. If this empirical α_{4-3} value is applied to the available data of (Pearson and Palmer, 2000) very different pH results emerge, increasing the magni-

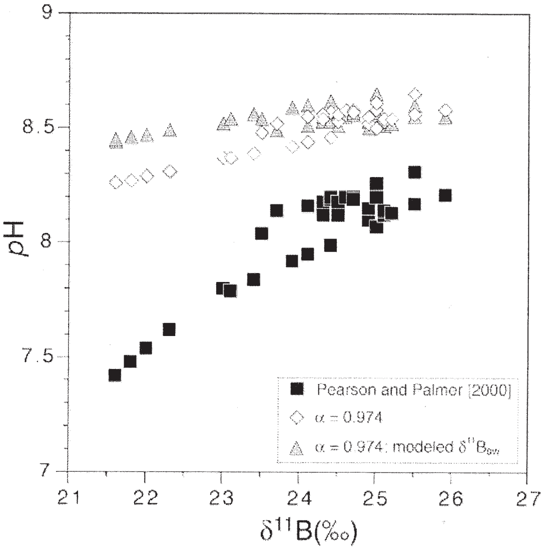

Fig. 7. pH estimates from the data of Pearson and Palmer (2000). Closed squares; results of Pearson and Palmer (2000), open diamonds; calculated using an α_{4-3} value of 0.974 and the modeled values of $\delta^{11}B_{sw}$ used in Pearson and Palmer (2000), shaded triangles; calculated using an α_{4-3} value of 0.974 and modeled values of $\delta^{11}B_{sw}$ from Figure 4.

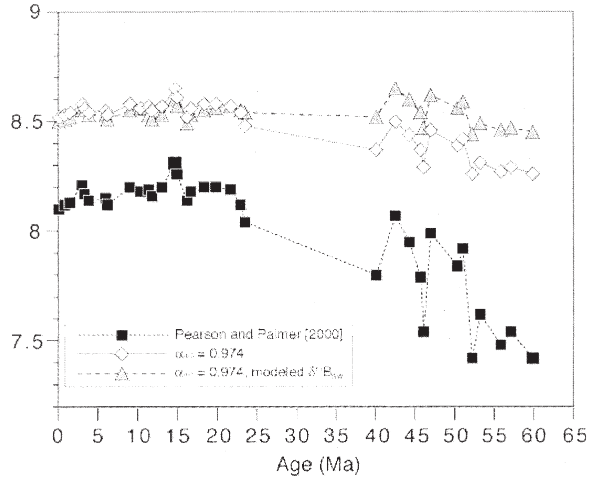

Fig. 8. Comparison of *p*H estimates. Closed squares; *p*H values of Pearson and Palmer (2000), open diamonds; *p*H values calculated from carbonate and seawater δ^{11}B values of Pearson and Palmer (2000), using an α_{4-3} value of 0.974, shaded triangles; *p*H values calculated from carbonate δ^{11}B values of Pearson and Palmer (2000), using an α_{4-3} value of 0.974 and $\delta^{11}B_{sw}$ values of Lemarchand et al. (2000; 2002).

tude of *p*H and reducing its range (Fig. 7). Although this re-estimated long-term *p*H trend suggests that the ocean is well buffered from potentially large changes in pCO_2, *p*H values are unrealistically high and inaccurate for the late Neogene. Further uncertainty is introduced as different models of $\delta^{11}B_{sw}$ are applied (Fig. 7) and vital effects are considered (Fig. 8).

Given the current state of our knowledge, vital effects of extinct species are likely to have occurred and need to be considered as inherent uncertainties in any *p*H reconstruction. It is possible that the appearance of high *p*H values during the Neogene result, in part, from species-specific vital effects. A small correction (~0.05 *p*H) can be applied to the Neogene because δ^{11}B values were measured from *Globigerinoides trilobus*, a close relative of *Globerigerina sacculifer* for which culture experiments have been performed. This correction slightly lowers estimated *p*H values, however, the resulting calculated *p*H for the Neogene remains unrealistically high relative to the Present.

7. CONCLUSIONS

The boron isotope-*p*H proxy is currently based on a theoretical model of carbonate δ^{11}B variation with *p*H. This model assumes that the boron isotopic composition of carbonates is isotopically identical to the boron isotopic composition of borate in solution. Understanding how the boron isotopic composition of borate changes with *p*H requires a precise definition of α_{4-3} and pK_B^*. If these assumptions and variables are valid and quantified, reconstruction of ancient ocean *p*H requires further knowledge of $\delta^{11}B_{sw}$, which is impacted by the rate of continental erosion. A review of the available data suggests that substantial uncertainty persists regarding the value of α_{4-3} and the history of $\delta^{11}B_{sw}$. Evaluation of carbonate δ^{11}B from inorganic precipitation experiments, assuming carbonate δ^{11}B is equivalent to the δ^{11}B value of $B(OH)_4^-$, indicate that the most appropriate value of α_{4-3} for carbonate systems is ~0.974 rather than the theoretical value of 0.981 from Kakihana et al. (1977). Compilation of available inorganic and culture experiments suggest that either the value of α_{4-3} is not constant with *p*H or that the supposition that carbonate δ^{11}B systematically reflects borate is faulty.

If the fundamentals of the boron isotope-*p*H proxy are assumed correct and the empirical value of 0.974 for α_{4-3} is applied to foraminiferal δ^{11}B values for the Cenozoic, *p*H reconstructions indicate little change in ocean *p*H over the Cenozoic. However, surface water *p*H values are unrealistically high for the Quaternary, and thus unlikely that these *p*H results are accurate.

The results of this exercise demonstrate that a wide range of *p*H is possible for a given carbonate δ^{11}B, and this range increases as the geological extent of reconstructions exceed the residence time of boron in the ocean. Complications aside, boron isotopes remain a potentially powerful tool in the reconstruction of past seawater *p*H, however, various aspects of boron systematics require rigorous evaluation. Therefore, given our current understanding, care should be taken when interpreting long-term trends in δ^{11}B when the ultimate goal is to reconstruct ocean *p*H and ancient atmospheric carbon dioxide levels.

Acknowledgments—The authors would like to thank E. Boyle and two other reviewers for critical reviews that helped improve the manuscript. Conversations with A. Sanyal, M. Wara, T. Bullen, A. Paytan, K. Turekian, B. Berner, W. Broecker, and J. Bijma were greatly appreciated and helped to shape the ideas presented within.

Associate editor: L. Kump

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