Marine biogeochemistries of Be and Al: A study based on cosmogenic ^{10}Be, Be and Al in marine calcite, aragonite, and opal

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The geochemical behaviors of Be and Al in ocean waters have been successfully studied in recent years using natural, cosmogenic, radioactive ^{10}Be and ^{26}Al as tracers. The present day dissolved concentrations and distribution of the stable and radioactive isotopes of Be and Al in ocean waters have revealed their short residence times and appreciable effects of exchange fluxes at the coastal and ocean-sediment interfaces. It follows that concentrations of these particle-active elements must have varied in the past with temporal changes in climate, biological productivity and aeolian flux of continental detritus to the oceans. We therefore investigated the feasibility of extending the measurements of Be and Al isotope concentrations in marine systems to the 10^3–10^6 y BP time scale. We report here the discovery of significant amounts of intrinsic Be and Al in marine foraminiferal calcite and coral aragonite, and of Al in opal (radiolarians) and aragonite (coral), which makes it possible to determine ^{10}Be/Be and ^{26}Al/Al in oceans in the past. We also report measured ^{10}Be/^{9}Be in foraminiferal calcite in Pacific Ocean cores, which reveal that the concentrations and ratios of the stable and cosmogenic isotopes of Be and Al have varied significantly in the past 30 ky. The implications of these results are discussed.

1. Introduction

Since the pioneering observations by Merrill *et al* (1960) of the very low concentrations of dissolved ^{9}Be in seawater, and those by Raisbeck *et al* (1979) of the ultra-low concentrations of dissolved ^{10}Be in the oceans, a large number of measurements have been reported for the concentrations of these isotopes in vertical profiles in the principal oceans (e.g. Kusakabe *et al* 1987; Ku *et al* 1990; Measures and Edmond 1990). The data base is extensive and throws considerable light on the marine geochemistry of beryllium as controlled by biology, climate and aeolian fluxes to the ocean. The advantage of making simultaneous measurements of ^{10}Be and ^{9}Be lies in the fact that the former is produced by cosmic rays, essentially at a constant rate (Lal and Peters 1967) and independent of climate, whereas the dissolved concentration of ^{9}Be depends on factors such as climate, marine biological productivity, and (aeolian) dust flux, the last two of which can be strongly coupled to climatic changes. Furthermore, absolute ^{9}Be (or ^{10}Be) concentrations in marine materials depend on ocean chemistry and temperature, but the ^{10}Be/^{9}Be ratio would be fixed in the proportion in the seawater. The ^{10}Be/^{9}Be ratios, rather than the absolute ^{9}Be concentrations, are therefore a better representation of changes in ocean chemistry because absolute ^{9}Be concentrations may display larger spatial variability.

In addition to Be, recent careful studies of dissolved concentrations of ^{26}Al and Al (which is represented effectively by ^{27}Al) in seawater (Ku *et al* 1995), have now added another paleo-tracer for studying the marine biogeochemistry of a second particle-active element with a cosmogenic isotope. The studies of Ku *et al* (op. cit.) revealed that Al is removed 30 times faster than Be from surface

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ocean waters, and that Al should serve as an ideal paleo-tracer for biological productivity.

Thus simultaneous studies of dissolved Be and Al marine isotope concentrations and ratios from ocean waters of the past seem promising for establishing changes in ocean chemistry and biological productivity. This paper reports the result of the first study to pursue this course of action. Prior to this work, no method had been developed for the study of paleo-concentrations of dissolved Be and Al isotope concentrations in ocean waters.

2. Background and previous work

The relatively short residence time of Be and Al in seawater due to their particle/bio-active nature, as well as the availability of their long-lived naturally produced radionuclides, ^{10}Be and ^{26}Al, is the principal reason why isotopic pairs of Be and Al are uniquely suited for high-resolution studies of paleoclimate, seawater-dissolved trace nutrient concentrations, and marine biological productivity. A feature of studies using this approach is that, considering the short residence times of Be and Al in seawater, their dissolved ocean concentrations must be significantly affected by temporal changes in aeolian dust flux, the source of dissolved Be and Al (Measures *et al* 1996) in seawater. During cold periods, winds are strong and the flux of aeolian dust that enters the oceans increases appreciably, as evidenced by the positive correlation of colder climates and increases in dust concentrations in polar ice cores. It is also known that directed temperature shifts can lead to climatic events such as El Niños and changes in tradewind strength, as well as changes in the character of both the thermohaline and wind-driven ocean circulation (Sarnthein *et al* 1988; Berger *et al* 1989; Summerhayes *et al* 1992, 1995; Lorius *et al* 1993; Raymo 1994; Mayewski *et al* 1996; Thompson *et al* 1997). Therefore, it would be expected that during cold climatic periods, non-cosmogenic Be and Al (i.e., ^{9}Be and ^{27}Al) fluxes to oceans would increase (while fluxes of cosmogenic ^{10}Be and ^{26}Al would remain unchanged). The increase in dust flux would be tied to an increase in supply of dissolved nutrients to surface seawater as a result of wind forcing. Although changes in isotope production are expected to occur from changes in the geomagnetic field, such perturbations are generally small (Lal and Peters 1967; Lal 1992). Direct measurements of ^{10}Be fluxes on the surface of the earth during the past ∼30 ky have been made by measuring ^{10}Be concentrations in well documented ice cores from the Greenland Summit (Finkel and Nishiizumi 1997; Yiou *et al* 1997). These data showed that the ^{10}Be fluxes were well constrained during the past 30ky, the period of interest in this study. The mean flux during the Holocene was $\sim 3.5 \times 10^5$ ^{10}Be atoms/cm^2/y, and $\sim 3.0 \times 10^5$ ^{10}Be atoms/cm^2/y during 10–30 ky BP. As a result, because the residence time of Al is about 30 times shorter than that of Be (Ku *et al* 1995), concentrations of ^{26}Al and ^{27}Al (with ^{27}Al being represented by total Al) would be affected more significantly than that of ^{10}Be and ^{9}Be (with ^{9}Be being represented by total Be).

To examine temporal changes in the dissolved concentrations of Be and Al isotopes in seawater in the past, we studied the intrinsic concentrations of Be and Al in three principal marine biogenic materials: calcite (foraminifera), aragonite (coral), and opal (radiolaria), using techniques to exclude signals from detrital Be or Al. These studies proved very rewarding since we discovered appreciable amounts of intrinsic Be and Al in the three biogenic matrices. This made it possible to analyze the dissolved concentrations of stable and cosmogenic Be and Al isotopes with respect to the principal matrix ingredient, Ca (in calcite and aragonite) and Si (in opal). Prior to this study, no data have been reported for Be and Al isotopes in marine calcite and opal with the objective of determining the isotopic ratios of Be and Al in seawater in the past. However, a few measurements have been reported for stable Be concentrations in coral and opal samples (Bourles *et al* 1984; Bourles *et al* 1989). Several measurements of Al in opal have been reported (Ellwood 1998), which were, however, not considered to be representative of the intrinsic Al concentrations in opal.

3. Experimental methods and samples

To identify suitable archives of the cosmogenic Be and Al isotopic records of seawater in the past, we analyzed three principal biogenic materials: foraminiferal calcite, coral aragonite, and radiolarian opal, all of which have been studied thoroughly over the past several decades for various trace elements that are indicative of changes in ocean chemistry, climate, and river inputs.

In the past decade, pioneering investigations on the marine geochemistry of Be and Al isotopes have been carried out by Kusakabe *et al* (1982, 1987), Measures and Edmond (1983, 1990), Bourles *et al* (1984), Ku *et al.* (1990), and Brown *et al* (1991). In processing our three potential Be/Al archive materials, we adopted standard procedures that have been set up for cleaning samples to remove all traces of detrital contamination (i.e., in foraminiferal calcite: Delaney and Boyle 1983, 1987; Lea and Boyle 1990; Elderfield 1990; Boyle

1992; in radiolarian opal: Shemesh *et al* 1988; Ellwood 1998; in coral aragonite: Shen and Boyle 1988; Linn *et al* 1990). Trace element concentrations (e.g., Cd, Ba, U, Ge) in solid residues left after cleaning were analyzed using an ICP-MS.

Repeated experimentation with calcite of different grain sizes demonstrated that sample sizes of ~ 2 g and mineral grains $> 63\mu$m could be satisfactorily cleansed of detrital aluminosilicate material following the procedures summarized below. Detrital clays were removed by repeated washing and ultrasonication of samples in hydrogen peroxide and calgon solutions. Using gravitational settling, this resulted in the near total removal of all fine-grained particles. During this process (~10 steps per sample) nearly 30–40% of sample was lost by discrimination and fragmentation. At the end, clear supernatants were obtained. The remaining cleansed solids were analyzed for total Be and Al. Repeat chemical analyses performed during sequential dissolution of the residual solids showed little compositional or isotopic variation, indicating that samples were effectively cleansed of all detrital materials. After cleansing, samples were dissolved in 25% acetic acid and centrifuged. One aliquot of solution was decalcinated by fluoridation and treated with HF, perchloric acid, and HCl. An aliquot of the sample was taken to be analyzed for ^{26}Al and was precipitated as Al_2O_3. An aliquot of sample to be analyzed for ^{10}Be was precipitated as BeO.

In the case of opal samples, we worked with samples which were >99% opal, with an appreciable mass in long spicules. The sieved material was cleansed of detrital material by repeated suspension in water (see also Ellwood 1989). Finally, size fraction >10 microns was retrieved (which contained most of the spicules), and processed for stable element analyses, by dissolution in very dilute HF at room temperature. This step was found to be quite mild for detrital matter.

To date, we have studied the stable isotopes of Be and Al in all the three biogenic materials, and a study of cosmogenic ^{10}Be in two foraminiferal calcite-rich box cores. Calcite samples for our present study come from two neighboring box cores from the equatorial Pacific Ocean taken during the Eurydice expedition (Berger and Killingley 1982). Opal samples were derived from the Ocean Drilling Program, Leg 177, Hole 1091A (47°5.681′S, 5°55.120′E), water depth 4360.5 mbs, from the Holocene section of the core. The coral sample was collected in 1990 under 10 m of water, near the town of Padang Bali on the southeast coast of Bali. Calcite and opal fragments were separated from the cores, cleansed off detrital clay, and analyzed for ^{10}Be following the procedure of Gu *et al* (1996) using the accelerator mass spectrometer at the Lawrence Livermore National Laboratory. Because cosmogenic isotopes are present in such low abundance, the concentration of the stable isotopes of Be and Al can be effectively represented by total elemental values. These were obtained for our samples in our laboratory using an ICP_MS.

4. Results and discussion

Determinations of Be and Al isotopic concentrations in the different marine materials studied are summarized in tables 1, 2, and 3. Table 1 has the data for both ^{10}Be and ^{9}Be (i.e., total Be). For stable Be concentration, there is a published value of $\sim 0.84 \pm 0.05$ ppb in a coral sample (C3), by Bourles *et al* (1984), which is in fair agreement with our values of 2.2 and 1.2 ppb (table 2). For opal there are three Be concentrations determined by Bourles *et al* (1989). These are listed in table 3. Our values are of the same order, but about 1.5–2× higher than those of Bourles *et al* (1989). Ellwood (1998) has determined several Al concentrations in opal samples. They ranged between 600 and 2800 ppm Al, which should be compared with our values of 860 and 1000 ppm Al in the two opal samples analyzed by us (table 3).

It can be shown from simple theoretic considerations that it is extremely unlikely that we have any significant contamination of Be and Al due to detrital materials in our cleansed calcite and opal samples. We start with the reasonable assumption that the maximum amount of detrital material we could leave in the cleansed sample is $< 0.1\%$ clay. Such amounts if present would become easily manifest in any sample suspension experiment. (As was mentioned, we discard light suspended materials by repeat suspensions till we obtain totally clean supernatants). There may be some detrital materials trapped in the forams, but these would of course be at much lower levels! Taking a value of 5 ppm Be in detrital materials (clay etc), this corresponds to < 5 ppb Be as the upper limit for the contamination level of Be in calcite or opal. Adopting a value of 2 for SiO_2/Al_2O_3 ratio in the clay and a molecular weight of ~ 300 g mol^{-1} for marine clays (Shemesh *et al* 1988), we expect levels of contamination from detrital materials present at concentrations of 0.1% in the calcite/opal samples to be < 200 ppb Al. The expected values of 5 and 200 ppm Be and Al respectively are certainly upper limits for the contributions from detrital materials since all the detrital material present in the sample would not be expected to dissolve in the dissolution step!

Table 1. *Measured concentrations of intrinsic* ^{9}*Be and* ^{10}*Be, and* ^{27}*Al in foraminiferal calcite from the equatorial Pacific Ocean ERDC box-cores ERDC 125 and ERDC 135, Lat. 0° S, 1° N, Long. 161° E/Lat. 0° 52'N, Long. 161° E, respectively; water depth = 3420–3430 m.*

		Approx.		Concentration in calcite			
Code	Depth (cm)	^{14}C age$^{(a)}$ (ky)	Grain size (μ m)	^{27}Al (ppb)	^{9}Be (ppb)	^{10}Be (10^{7} atoms/g)	^{10}Be/^{9}Be ratio (10^{-7} atom/atom)
ERDC1	0 – 5	2.0	63 – 300	30	5.9	1.21 ± 0.043	0.31 ± 0.038
ERDC3	0 – 5	2.0	300 – 500	13	11.9	0.75 ± 0.014	0.096 ± 0.012
ERDC4	8 – 11	5.5	>63	42	42.4	1.03 ± 0.023	0.036 ± 0.005
ERDC5	11 – 13	6.4	>63	105	40.9	1.90 ± 0.021	0.069 ± 0.009
ERDC6	15 – 20	11.0	>63	155	49.9	1.00 ± 0.031	0.031 ± 0.004
ERDC7	35 – 40	18.0	>63	99	41.4	1.03 ± 0.033	0.037 ± 0.005
ERDC8$^{(b)}$	31 – 33	25.0	>63	45	12.6	0.52 ± 0.210	0.062 ± 0.025
ERDC9$^{(b)}$	39 – 42	30.0	>63	24	27.2	0.79 ± 0.043	0.043 ± 0.005

(a) ^{14}C ages are based on tree ring calibration, but have not been corrected for reservoir effect, the neglect of which overestimates the ages by about 0.5 ky.

(b) Samples ERDC8 and ERDC9 are from core ERDC 135; samples ERDC1 thru ERDC7 are from box core ERDC 125.

Table 2. *Measured concentrations of Be and Al in recent biogenic foraminifera- calcite and coral-aragonite.*

	Concentration			
Code	Be (ppb)	Al (ppb)	Be/Ca (atom/atom)	Al/Ca (atom/atom)
1. Calcite (foraminifera)				
ERDC (0-5 cm)				
Recent (Table 1)	$\sim 10^{(a)}$	$\sim 20^{(a)}$	$\sim 10^{-7}$	$\sim 10^{-7}$
2. Coral (aragonite)				
Coral 1	2.2	820	2.5×10^{-8}	3.0×10^{-6}
Coral 2	1.2	230	1.3×10^{-8}	8.6×10^{-6}

(a) Approximate average of 0–5 cm samples in table 1.

Table 3. *Measured concentrations of Be and Al in diatom opal.*

	Concentration				
Code	Be (ppb)	Al (ppb)	Be/Si (atom/atom)	Al/Si (atom/atom)	Reference
Opal 1	220	10^{6}	1.5×10^{-6}	2.2×10^{-3}	Present work
Opal 2	154	8.6×10^{5}	1.0×10^{-6}	1.9×10^{-3}	Present work
Opal RC 11 – 78, 10 cm	81	-nm-	5.4×10^{-7}	-nm-	(Bourles *et al* 1989)
Opal RC 12 – 65, 262.5 cm	56	-nm-	3.7×10^{-7}	-nm-	(Bourles *et al* 1989)
Opal AET 7606, surface	130	-nm-	8.7×10^{-7}	-nm-	(Bourles *et al* 1989)

-nm- = not measured.

Furthermore, the ratio of Al/Be in the sample arising from detrital materials is expected to be of the order of 40. We note that the measured Al/Be ratios in calcite (table 1) and opal (table 3) are in the range of (1–6) and ~ 5000 respectively. In two coral samples analyzed (table 3), the Be/Al ratio lies in the range, 200–400. This wide variation in the Al/Be ratios in the calcite, opal and aragonite samples does seem to strengthen our conclusion that the measured Be and Al concentrations are not dominated by the presence of any detrital material present in our cleansed samples, and that the ratios reflect the intrinsic property of the biogenic mineral studied. Further support for this statement comes from the fact that in calcite where we have measured ^{10}Be/^{9}Be ratios, the ratios in recent calcite samples are close to the ^{10}Be/^{9}Be ratios observed in near surface sea waters, as discussed below.

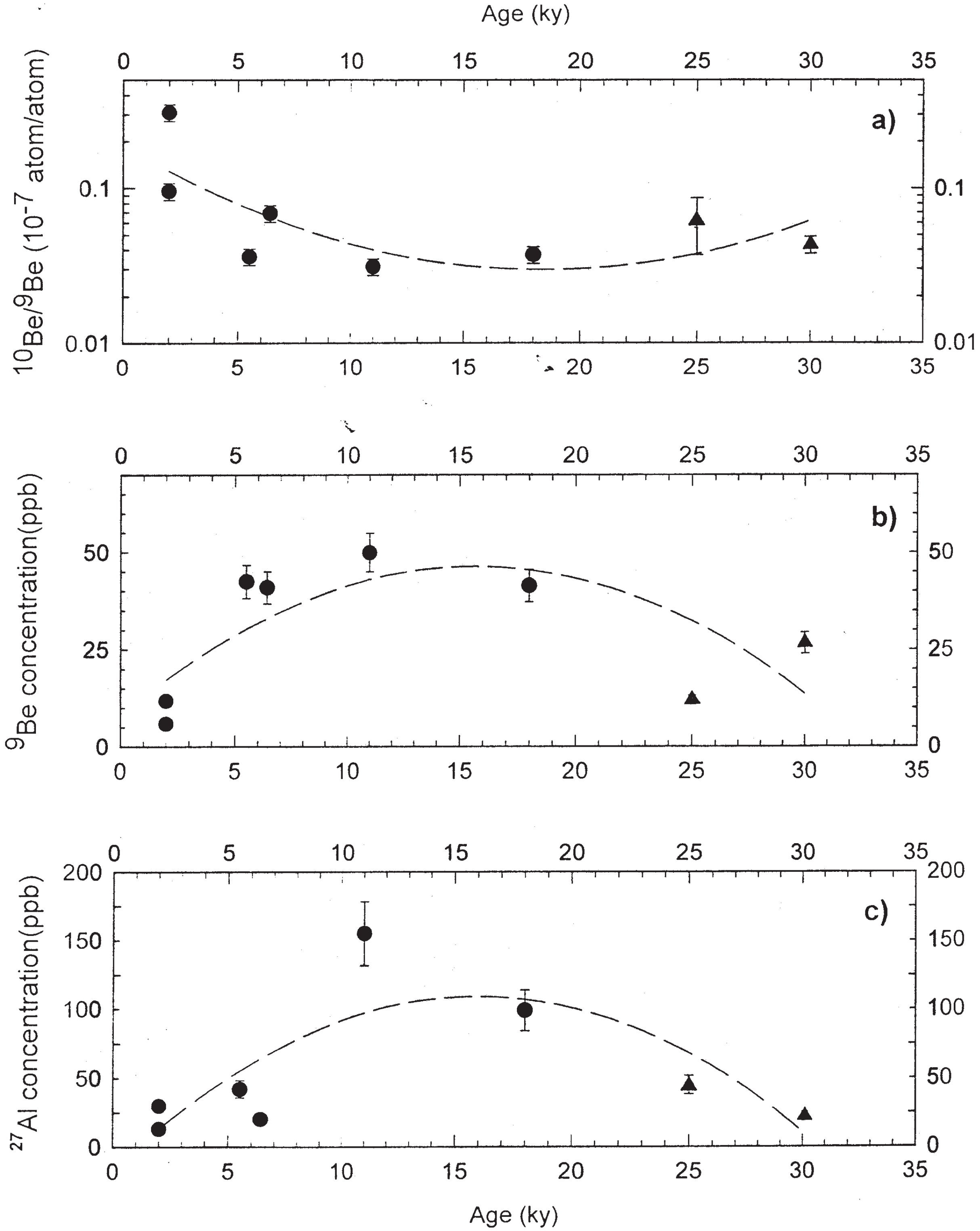

Figure 1. Measured concentrations of intrinsic Be, Al and ^{10}Be concentrations in foraminiferal calcite from the equatorial Pacific Ocean box cores ERDC 125 (circles) and ERDC 135 (triangles); for details see table 1.

Following an important comment by one of the reviewers, we examined several samples of opal and foraminiferal calcite, bulk and processed, under the SEM, for the presence of Fe or Mn coatings. All biogenic particles were pristine and no evidence was found for coatings. EDS spot analyses and chemical maps did not reveal the presence of any appreciable concentrations of either element which would indicate the occurrence of coatings on the particles.

It can be seen from table 1 that ^{10}Be is easily measured in foraminiferal calcite samples. Further, data in tables 2 and 3 clearly show that sufficient amounts of cosmogenic ^{10}Be and ^{26}Al are present, with sufficiently small uncertainties, in coral aragonite and in diatom to permit meaningful measurements.

To judge the suitability of our selected biogenic materials as archives for dissolved Al and Be in seawater, and thus as proxies for trace nutrients derived from the dissolution of windblown detrital minerals, the intrinsic elemental Be and Al concentration data obtained from core tops (0–5 cm) in our modern samples were compared with estimates of the present average elemental concentrations in seawater (tables 1–3). Seawater values adopted for our comparison studies are the average values reported in the literature for modern Pacific Ocean surface waters in units of moles per liter (M): Be = 10 pM and Al = 2 nM (Kusakabe *et al* 1982, 1987; Measures and Edmond 1983, 1990; Ku *et al* 1990, 1995; McHargue and Damon 1991; Brown *et al* 1991), and Ca = 10 mM; and Si = 10μmol (Riley and Chester 1971). A comparison of these average modern-day seawater values with those in tables 2 and 3, obtained from our biogenic archives, reveal the following:

- In foraminiferal calcite, *relative to Ca*, Be is enriched by a factor of ∼100 over that in seawater and Al is depleted by a factor of about 3. Both Be and Al are included in appreciable concentrations in the calcite matrix, as is also seen by the positive correlation between Be and Al (figure 1b and c).
- In coral aragonite, *relative to Ca*, Be is enriched by a factor of ∼ 20 over that in seawater and Al is enriched by a factor of ∼ 10.
- In radiolarian opal, *relative to Si*, Be is neither enriched nor depleted compared to seawater, but Al is enriched by a factor of about 10, as in corals.
- The ^{10}Be/^{9}Be ratios of present-day surface ocean waters (Kusakabe *et al* 1987; Ku *et al* 1990; McHargue and Damon 1991), are comparable to the ^{10}Be/^{9}Be ratios in foraminiferal calcite (table 1).
- Figure 1(a, b, and c) respectively, show plots of ^{10}Be/^{9}Be ratios, as well as ^{9}Be and ^{27}Al concentrations with their uncertainties for the ERDC box cores. Values in table 1 show considerable variation, by an order of magnitude, during 30 ky BP, illustrating that the dissolved concentrations of continentally derived Be and Al change significantly with time, thereby providing a potentially sensitive chemical indicator of global change.

These results suggest that foraminiferal calcite and coral aragonite are excellent repositories for paleo-concentrations of seawater dissolved Be. For dissolved Al, coral aragonite and diatom opal are both satisfactory. Of the three, coral occupies the middle range for suitability for determining both Be and Al concentrations. Calcite, however, is not useful for determining concentrations of dissolved Al.

As shown in figure 1, there is an inverse relationship between ^{10}Be/^{9}Be and the intrinsic trace element concentration of ^{9}Be. Our study also shows a similar relationship for ^{10}Be/^{9}Be and ^{27}Al concentrations. Unfortunately in our data set there are large time gaps between points. As a result, the actual shape of oscillations and the fine structure of the curves in figure 1(a, b, and c) have not yet been determined. Nevertheless, fitting the data with a second order polynomial yields a crude minimum in ^{10}Be/^{9}Be ratios and a maximum in ^{9}Be and ^{27}Al concentrations at 15–20 ky BP. These data structures are in reasonable agreement with the end of the last glacial maximum (∼ 20 ky BP) when the global climate was significantly cooler than today. Low ^{10}Be/^{9}Be ratios should be expected during times of intense glaciation owing to increased wind forcing that is generally tied to cooler climatic conditions. This wind forcing increases the continental dust flux to the oceans, resulting in the dilution of cosmic ray-generated ^{10}Be with ^{9}Be. We feel that the overall lower ^{10}Be/^{9}Be ratios of samples older than 15 ky are intriguing and appear to link the Be and Al contents of foraminiferal calcite directly to well-documented climatic (and wind) forcings that are known to have occurred during recent glacial eras. Of further interest is that these low ratios also correspond with observed increases in paleoproductivity (Berger and Killingley 1982).

Although similar isotopic ratios have yet to be collected for Al and for Be in the other marine biogenic materials studied (coral aragonite and radiolarian opal), the presence of cosmogenic ^{9}Be and ^{27}Al and reasonable concentrations of total Be and Al in these materials (tables 2 and 3) would suggest that similar data sets from these materials can also be generated.

5. Conclusions

Our results clearly establish the dramatic possibility of studying the paleogeochemistry of seawater with stable and cosmogenic Be and Al isotopes using biogenic calcite, aragonite and opal. One important result of our work is that we have shown that with the present day sensitivity of 10^6 atoms for ^{10}Be and ^{26}Al, and with dissolved ^{10}Be/Be and ^{26}Al/Al ratios in the range of 10^{-8}–10^{-7} and 10^{-13}–10^{-14}, measurable amounts of ^{10}Be can now be detected in < 1 to a few grams of modern calcite or opal. Similarly, ^{26}Al can be detected in 1–5 g of modern opal. This high sensitivity makes it possible to now carry out paleoceanographic studies of Be and Al in a variety of marine sediments.

Our study also indicates that the isotopic ratios of Be and Al can shed valuable light on how and why ocean productivity has varied in the past—a key to understanding climate controls, and burial of organic matter in the oceans. Full-scale validation of our admittedly sparse data set has the potential to open up new avenues for quantifying biological productivity variations and their ties to continental dust flux and its effect on boosting the dissolved nutrient content of seawater. This, in turn, can be related quantitatively to organic matter preservation in sediments and, thus, improve our understanding of the carbon cycle and its change over time. A bonus of our technique is that because Be and Al ratios are tied to wind forcing, they should also serve to couple changes in tradewind strength, thus paleoclimate, and ocean paleoproductivity. This resulting new window into the past will hopefully establish new links to cause-effect scenarios, e.g. climate and ocean circulation, atmospheric carbon dioxide concentrations and climate, etc.

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