

Analyses of proteins in natural carbonates: Recent aragonitic ooids, Great Bahama Bank

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Introduction

Amino acids have previously been identified in a variety of non-skeletal carbonates. However, the methods used for identification do not distinguish between amino acids that are free in solution versus amino acids that are covalently linked into a peptide or protein. Proteins cannot be easily formed abiotically and, thus, the identification of a protein in a carbonate would signify that the carbonate is either skeletal in nature or contains a remnant of a deceased organism from the vicinity.

Results

Three proteins were identified in aragonite ooids from the Bahamas Bank using gel electrophoresis. The proteins have apparent molecular weights larger than 55,000 g/mol. The first fifteen amino acids of the most abundant protein was sequenced by N-terminal sequencing. The sequence, however, did not match any protein in the current protein databases. This indicates that the proteins are not a result of human contamination (since the sequences of human skin and hair keratin are in the database) and the protein has either not been entered into the database, has not yet been identified, or the protein has been degraded beyond recognition. Two species of *Halimeda*, a prolific organism in the Bahamas platform, were compared to the ooid sample. *Halimeda* extracts contain proteins of molecular weights similar to the ooids and may be the source of the proteinaceous material.

Conclusions

These results indicate that not only free amino acids but intact proteins may be incorporated into non-skeletal carbonates. The proteins may even serve as a template for deposition and, therefore, facilitate the process.

Li isotopic systematics of volcanic rocks in marginal basins

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Li isotopic data may provide useful information on material behaviours through the subduction process. The Li isotopic compositions of volcanic rocks from the convergent plate margins differ from those of the divergent boundaries: the $\delta^7\text{Li}$ values ($\delta^7\text{Li}$ (‰) = $([^7\text{Li}/^6\text{Li}]_{\text{sample}}/[^7\text{Li}/^6\text{Li}]_{\text{L-SVEC standard}} - 1) \times 1000$) of many magmatic arc lavas range between those of fresh MORB (ca. +4‰) and those of subducted components ($\delta^7\text{Li} > +10\%$) such as altered oceanic crusts and marine sediments, which may be explained by the mixing of these two components [1]. Chan et al. [1] has reported that the $\delta^7\text{Li}$ values of several lavas from the Central American volcanic arc range $> -3\%$, which are significantly lower than the fresh MORB value (ca. +4‰). In addition, Chan et al. [1] has reported that the $\delta^7\text{Li}$ value of back-arc basin basalts (BABB) from Lau basin are +1.7‰ and +0.5‰, which are slightly lower than the fresh MORB value (ca. +4‰). Such low $\delta^7\text{Li}$ values cannot be explained by above-mentioned simple mixing model. To resolve the origin of negative $\delta^7\text{Li}$ source, we have analyzed Li isotopic ratios of volcanic rocks in several marginal basins, with Sr, Nd, He, Ar, C and N isotopic ratios.

Li isotopic ratios of volcanic samples have been analyzed using the second-generation multiple-collector ICP mass spectrometry [2]: The analytical error of our $\delta^7\text{Li}$ values is within $\pm 0.82\%$ (2σ). Analyzed fresh quenched glasses were recovered from three Pacific back-arc basins (North Fiji basin, Manus basin, and Mariana Trough).

There were correlations between the $\delta^7\text{Li}$ values and the $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and La/Sm ratios. These results show that the N-MORB-like depleted BABB glasses (low- $^{87}\text{Sr}/^{86}\text{Sr}$, high- $^{143}\text{Nd}/^{144}\text{Nd}$, and low-La/Sm ratios) have low- $\delta^7\text{Li}$ values, in comparison with enriched back-arc volcanic glasses (high- $^{87}\text{Sr}/^{86}\text{Sr}$, low- $^{143}\text{Nd}/^{144}\text{Nd}$, and high-La/Sm ratios). The $\delta^7\text{Li}$ values of N-MORB-like BABBs, whose chondrite normalized La/Sm ratios are less than 1, are $+2.3 \pm 0.4\%$ (1σ , n=10). To estimate the $\delta^7\text{Li}$ value of N-MORB, we have also measured fresh MORB glasses that were recovered from Mid-Atlantic and Indian Ocean. The results show that $\delta^7\text{Li}$ values of N-MORBs, whose chondrite normalized La/Sm ratios are less than 1, are $+3.2 \pm 0.7\%$ (1σ , n=8). Accordingly, $\delta^7\text{Li}$ value of the mantle end-member source (most uncontaminated by the recycled components) in mantle wedge is lower than those of the upper mantle.

[1] Chan et al. (1999), Chem. Geol. 160, 255-280.

[2] Nishio & Nakai (2002), Anal. Chim. Acta 456, 271-281