Geochemistry of Precambrian carbonate intercalated in pillows and its host basalt: implications for the REE composition of circa 3.4 Ga seawater

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Abstract

The REE composition of early Archean seawater has been estimated through analyses of dolomite intercalated in pillow basalts from the Pilbara Block, Western Australia. We have critically evaluated the possible disturbances that have affected the chemical composition of the carbonate through geologic time. Dolomite samples from the Pilbara show a chondrite-normalized LREE-enriched pattern with profound downward convex tetrad effects, suggesting that these REE signatures are related to ancient seawater from which the dolomite precipitated. Contribution of a hydrothermal component to the seawater signature appears negligible based on the small Eu anomalies observed in dolomite. Therefore, dolomite samples from the Pilbara Block appear to preserve REEs intrinsic to ancient seawater, suggesting that the REE composition of seawater could be estimated given that carbonate–seawater partition coefficients of REEs are known. We used REE partition coefficients based on the analyses of a dolomite reference sample (JDo-1 from the Geological Survey of Japan) and show that REE concentrations of ∼3.4 Ga seawater could have been one or two orders of magnitude higher than at present. Moreover, it appears that 3.4 Ga seawater was significantly enriched in HREE and had less pronounced W-type tetrad effects relative to that of present seawater. These may reflect paleo-environmental conditions particular to seawater in the Archean, such as high-salinity and [CO3 2−].

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Keywords: Pilbara Block, Ankeritic dolomite, Rare earth elements, Archean seawater, Lanthanide tetrad effect

1. Introduction

The elemental and isotopic composition of ancient seawater is of great interest in deciphering the paleoenvironmental conditions of the Earth. Chemical
sediments, such as limestone and banded iron formation (BIF), have been an important source of information because they are believed to record the isotopic and trace elemental composition of ancient seawater from which they precipitated (Veizer and Compston, 1974, 1976; Burke et al., 1982; Veizer et al., 1989a, 1989b, 1992; Koeppnick et al., 1990; Hall and Veizer, 1996; Khan et al., 1996; Kato et al., 1998). Limestones and calcareous microfossils are particularly useful in obtaining the Sr isotopic composition \(^{87}\text{Sr}/^{86}\text{Sr}\) of ancient seawater since the Archean (e.g. Veizer and Compston, 1974; Burke et al., 1982; Palmer and Elderfield, 1985; DePaolo and Ingram, 1985; Veizer et al., 1989a, 1989b, 1992, 1999; Koepnick et al., 1990; Hall and Veizer, 1996; Khan et al., 1996; Kato et al., 1998). A series of studies on Sr isotopic composition of Precambrian carbonates by the Veizer and co-workers revealed that Archean carbonates have low \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios indistinguishable from that in the upper mantle deduced from mafic volcanic rocks. As for rare earth element (REE) compositions, BIFs may also provide valuable information on the geochemical composition of the Archean seawater (e.g. Fryer, 1977; Graf, 1978; Derry and Jacobsen, 1990; Bau and Möller, 1993; Gnaneshwar Rao and Naqvi, 1995; Khan et al., 1996; Kato et al., 1998). However, because BIFs commonly show distinct and ubiquitous positive Eu anomalies in their REE patterns (normalized to NASC), they appear to have been strongly affected by hydrothermal fluid input. Therefore, to obtain the REE signature of average ancient seawater from banded iron formation chemistry is problematic.

Archaean carbonates may be an alternative source of information for obtaining the geochemical composition of ancient seawater. Despite this reasonable expectation, REE data from Archean carbonates are rarely reported compared to those from BIF. This is probably because of their relative rarity and susceptibility to secondary alteration, which should affect the intrinsic REE signatures.

In order to elucidate whether Archean carbonates can be a valuable source of information on the geochemistry of ancient seawater, we have carried out analyses of major element and REE compositions of submarine pillow basalt and ankeritic dolomite intercalated in pillows, collected from within the Pilbara Block, Western Australia. These dolomites are very poor in detrital clastic sediments, and are thus expected to be suitable for studying the intrinsic geochemical signatures of Archean seawater.

Major and trace elemental compositions of the dolomites are compared to those of intercalated pillow basalts to evaluate the scale of element exchange between basalts and the carbonates. After critically evaluating the possible secondary effects on REE compositions of the carbonates, we show that REE composition of the carbonate is likely to preserve some information of the ancient seawater from which they precipitated using the partitioning coefficients between seawater and an independent dolomitic reference material.

2. Location and sample description

The Pilbara Block comprises granitoid–gneiss complexes and intervening belts of shallowly dipping to tightly folded volcanic and sedimentary rocks that are metamorphosed to lower greenschist facies (Fig. 1; Krapez, 1993). Greenstone belts of the Pilbara Block are divided into the Warrawoona Group, Gorge Creek Group, De Grey Group, and Whim Creek Group, in ascending order (Table 1; Hickman, 1983; Horwitz, 1990; Krapez, 1993). We examined pillow basalt sample from

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Stratigraphy of Warrawoona Group, Pilbara Block, modified from Hickman (1983), Horwitz (1990) and Krapez (1993)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group</strong></td>
<td><strong>Subgroup</strong></td>
</tr>
<tr>
<td>Warrawoona</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Taiga Taiga</td>
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</table>
Fig. 1. Sampling point of pillow basalt and intercalating ankeritic dolomite from Pilbara Block, Western Australia. Geological map is after Hickman (1983). The block of pillow basalt with about 2 m diameter (a) is collected for the purpose of exhibition at Nagoya University Museum. Analyzed samples (c) were cut from the subdivided block (b) of 45 cm (L) × 5–25 cm (W) × 4 cm (D).

3. Analytical methods

3.1. Basalt

Analytical results are shown in Table 2. The pillow basalt shows a compositional change of major elements following the Euro Basalt Formation. The formation has a thickness of about 2 km and is composed of pillow basalt with minor chert and felsic lava. According to Krapez (1993), the duration of the Warrawoona Megasequence Chronozone is estimated to be 150 m.y., from a lower limit of 3490 Ma to an upper limit of 3430 Ma. Thus, the age of Euro Basalt Formation is estimated to be about 3430 Ma. Euro basalt has been metamorphosed to varying degrees, but metamorphism was largely unaccompanied by high strain, so that original structures and textures are commonly well preserved. We collected a ∼2 m diameter pillow basalt block at Pillow Hill (Point 2 in Sugitani, 1992) at an outcrop (S20°49′, E119°31′) along the Northern Highway (Route 138). This particular pillow basalt block is on display at the Nagoya University Museum.

Vugs contained within the pillow basalt samples are filled mainly with carbonate (Fig. 1a and b). We cut a basalt-carbonate block into 11 chips with a diamond saw; five of these chips are dominantly composed of basalt and the rest consist of carbonates (Fig. 1c). X-ray diffraction (XRD) analyses show that the pillow basalt is composed mainly of chlorite and quartz with minor amounts of mica and calcite (?). The CO2 effervescence by diluted HCl treatment confirms the presence of a carbonate phase. Olivine, clinopyroxene and plagioclase appear to have been completely altered to clay minerals.

Microscopically, carbonate samples contain calcic dolomite in which the original calcite has been almost totally replaced by an unstrained loose interlocking of euhedral dolomite crystals. The contact between basalt and carbonate is relatively sharp and detrital grains were absent at the contact. This suggests that the carbonate was emplaced soon after pillow basalt formation. On the other hand, carbonate minerals are observed to occur in cavities of the pillow basalt. Dolomite identified in the pillow basals is unstrained and occurs as almost euhedral rhomb-shaped small crystals (ca. 10 μm), which contain cloudy inclusions of probable calcite.

For REE determinations, 0.1 g of carbonate sample was digested with 1.7N HCl under mild heating (<60 °C) until CO2 effervescence ceased. For basalt samples, about 0.1 g was digested with 3 ml HF and 1 ml HClO4 on a hotplate at 180 °C until dryness, and dissolved with 2 ml 1.7N HCl. After centrifugation, supernatant solutions for both basalt and carbonate samples were applied to conventional column separation (Dowex 50W×8). REE compositions were determined with HP4500 inductively coupled plasma mass spectrometer (ICP-MS). Standard solutions were prepared by mixing of respective REE solutions. Interferences of oxide ions of light REEs on heavy REEs were corrected applying respective oxide factors of LREEs determined by measurement of 20 ppb LREE solutions. Indium and Bi were used as internal standards.

In order to monitor analytical precision of REE analyses and determine partition coefficients between dolomite and seawater, GSJ dolomite reference rock (JD0-1) was also analyzed repeatedly by the same procedure together with the carbonate samples.

4. Results

4.1. Major and minor element composition

4.1.1. Basalt

Analytical results are shown in Table 2. The pillow basalt shows a compositional change of major elements
from core (No. 2) to rim (No. 5); the rim is enriched in SiO₂ and K₂O and depleted in MgO and Fe₂O₃ compared to the core (Fig. 2). Enrichments of SiO₂ and K₂O were also observed in acidic rocks from Wyman Formation and are interpreted as a result of hydrothermal alteration at low temperatures (Barley, 1984). It was also documented that most of the Salgash Subgroup (including the Euro Basalt) is strongly altered and that such alteration is most significant in originally porous units such as pillow flows (Berley, 1993). Therefore the observed excess in SiO₂ and K₂O towards the rim of our pillow basalt is probably due to hydrothermal alteration. In contrast to those hydrothermally modified elements, Al₂O₃/ThO₂ ratios in sections of the basalt (except for slightly lower Al₂O₃/ThO₂ in the rim) appeared to be relatively constant (Fig. 2). This is consistent with

The "tr" means below detection limit, and "Ig. loss" does loss on ignition

* Data of Euro basalt are quoted from Hickman (1983).
Fig. 2. Compositional changes of major elements across the pillow basalt. Based on the elemental profile, No. 2 is considered to be the center of the pillow.

The previous notion that these two elements are quite conservative towards secondary alteration (Yamamoto et al., 1986; Sugitani et al., 1996; Polat and Hofmann, 2003).

Another significant feature of the major elemental chemistry of the basalt sample is that it contains significantly lower amounts of CaO and Na2O compared to literature data. The observed CaO concentrations of \( \sim 0.5\% \) are much lower than those reported elsewhere for the Euro Basalt (8.34 wt%, average of 16 Euro Basalts from many locations by Hickman, 1983). Moreover, no samples yielded detectable Na2O by XRF (2.04 wt% on average; Hickman, 1983). The depletion of these elements may also be ascribed to the effects of hydrothermal alteration.

A record of ancient mantle melting can also be found in their relatively high concentrations of transitional elements (Cr, Co and Ni) compared to Phanerozoic equivalents. These high concentrations of transition elements in Archean basalts probably reflect the higher degree of partial melting of the mantle source under higher mantle temperature in Archean (Condie, 1985).

4.1.2. Carbonate

In contrast to the observed chemical gradients in the basalts, no clear chemical heterogeneity can be seen among the carbonate samples, except for high SiO2 concentration of No. 6 carbonate, which is in direct contact with the pillow basalt. The XRD spectrum shows that the carbonate rocks are composed mainly of dolomite. However, the relatively high concentrations of 4–5% FeO and 1.4% MnO (Table 2) indicate an important ankerite component, \((\text{Ca, Fe, Mn})\text{CO}_3\), in the carbonate samples. According to Veizer et al. (1989a), carbonates in the older greenstones (\(\sim 3.5 \pm 0.1 \text{ Ga} \)) are predominantly ferroan dolomites with some affinity to hydrothermal dolomite. Hereafter, we refer to the carbonate in our samples as ‘dolomite’.

4.2. Rare earth element composition

Fig. 3. REE patterns of basalt samples normalized to CI-chondrite. Normalizing values are mainly quoted from Anders and Grevesse (1989). Shinotsuka et al. (1995), pointed out that the REE patterns of chondritic samples show a zigzag pattern in the CI-normalized HREE region. It was suggested that such a zigzag pattern is attributable to isotopically high abundances of mono-isotopic REE (Tb, Ho and Tm) in the CI values. Therefore, normalizing Tb, Ho and Tm concentrations of 0.0348, 0.525 and 0.0234 ppm (Ebihara, pers. comm.) were used instead of 0.0363, 0.0556 and 0.0242 ppm by Anders and Grevesse (1989), respectively.
Fig. 4. REE patterns of carbonate samples normalized to CI-chondrite. Normalizing values are the same as those described in the text. Cerium and Pr plot downward from a straight line connecting La and Nd. The same holds true for Gd–Ho span. These observations suggest carbonate samples reflect a lanthanide tetrad effect.

Tsikos et al., 2001). NASC and PAAS indeed have distinct negative Eu anomalies when normalized against the chondritic value; thus we consider normalization by already fractionated compositions as somewhat misleading. Modifications of chondritic values by Ebihara (pers. comm.) are stated in the figure caption.

4.2.1. REE in the basalt
As shown in Fig. 3, when normalized to chondritic compositions, all basalt samples show light-REE (LREE) enriched smooth patterns with flat parts from La to Nd and from Ho to Lu, without Eu anomalies. Therefore, Eu fractionation by plagioclase had not occurred during the generation of melts that formed pillow basalt. Note that partial melting of a mantle with chondritic composition should produce melts with higher chondrite-normalized abundances of La than those of Ce, because La is more incompatible than Ce (Haskin, 1984). However, the basalts show low (La/Ce), ratios (0.937–0.979), except for sample No. 3. According to Polat and Hofmann (2003), LREEs are mobile during carbonate alteration of Precambrian basalts. The depletion of La relative to Ce may have been caused by the LREE loss during strong carbonate alteration. However, Polat et al. (2002) proposed that the presence of large Ce anomalies on primitive mantle normalization diagrams be adopted to assess the effects of alteration. Although CI-chondrite is used for normalization in this study, there were no apparent Ce anomalies observed. We propose that instead of alteration processes, the basalts might have been derived from a mantle domain that experienced depletion before 3.4 Ga ago.

Although the REE patterns seem to be parallel, LREE enrichment (expressed as (La/Yb)\textsubscript{n} ratios in Table 2) vary from 4.6 to 9.7 without obvious correlation with sampling position from the pillow, suggesting heterogeneous distribution of REE. Among basalt samples, No. 5 has the lowest REE concentrations compared to the other four samples. We noted above that No. 5 was the sample with the highest SiO\textsubscript{2} (~70%), suggesting that the low REE concentration is due to dilution by secondary quartz.

4.2.2. REE in the dolomite
The most significant feature in REE patterns of the dolomites is the presence of a W-type lanthanide tetrad effect (Masuda and Ikeuchi, 1979; Masuda et al., 1987). As shown in Fig. 4, the dolomite samples have generally LREE-enriched patterns with relatively unFractionated heavier REE (from Sm to Lu). However, these patterns are not as smooth as those of the basalt samples but show slightly concave trends defined at two portions: one between La and Nd and the other between Gd and Ho.

There are two types of tetrad effects for lanthanides in nature, termed W- and M-types according to their apparent shapes (Masuda et al., 1987). The W-type tetrad effect is conspicuous in modern seawater (cf. Fig. 6; Kawabe et al., 1998) and has also been reported in banded cherts from the Pilbara Block (Minami et al., 1995) interpreted as indicative of direct precipitation of the cherts from water. Thus, the occurrence of tetrad effects in the present samples suggests that the signal of ancient seawater could also be preserved in these Precambrian carbonates. Below, we focus on this interesting feature further.

5. Discussion
5.1. Secondary changes of REE composition of the dolomite
We have shown that Precambrian carbonates from Pilbara may provide information regarding the ancient
seawater geochemical composition. In order to further explore this possibility and discuss its implications, there are several issues awaiting clarification. It is important to note that the samples have been digested with 1.7N HCl under mild heating (<60 °C) to minimize potential contamination from fine-grained siliciclastic materials, which may be present within the carbonates phases (Banner et al., 1988). Moreover, the present carbonate samples contain only scarce quantities of silicates. Thus, the observed REE signatures of the dolomites are unlikely to be significantly influenced by non-carbonate phases. In our view, only (1) metamorphic events and (2) dolomitization processes could have disturbed the intrinsic REE signatures in the dolomites.

5.1.1. Metamorphic events

Minami et al. (1995), reported a Sm–Nd whole rock age of 2.5 Ga for the Marble Bar cherts and suggested that a significant thermal event occurred widely throughout the Pilbara Block. Jahn et al. (1981), also reported 2.3–2.4 Ga Rb–Sr ages for acidic rocks from the Panorama and Wyman formations, suggesting that the younger Rb–Sr ages represent the time of metamorphism associated with a widespread thermal event.

The most important question here is whether these metamorphic processes affected REE compositions of the dolomites. As mentioned, the basalt samples contain subordinate amounts of carbonate minerals as inclusions that fill cavities within the pillows (hereafter, to avoid confusion, the carbonates within the basalts will be called ‘carbonate-inclusions’). If the dolomite samples had equilibrated with the pillow basalt with respect to REE composition, carbonate-inclusions contained in the pillow basalt are expected to show the similar REE signature as that of the dolomite samples. To evaluate this possibility, we have analyzed Al and REE compositions of the carbonate-inclusions in the basalts (Nos. 4 and 5) by dissolving them with 1.7N HCl (Table 3). As shown in Fig. 5, the carbonate-inclusions have entirely different chondrite-normalized REE patterns not only from those of the pillow basalts but also from those of the dolomite phases. There are no signs of W-type tetrads effects in the carbonate-inclusions; instead, REE compositions of the carbonate-inclusions are characterized by profound enrichments in middle-REE (MREE). The REE pattern of carbonate-inclusion in the No. 5 basalts is also distinct from that of the dolomite sample (No. 6), despite the fact that these two samples are in direct contact with each other. Thus, the MREE-enriched patterns of carbonate-inclusions have probably resulted from equilibration with the host pillow basalt. Although the exact process responsible for the observed enrichment in MREE is difficult to speculate upon, an important point here is that signs of equilibration with the basalt are not found in the REE composition in the dolomite samples.
In the samples directly at the interface, their chondrite-normalized La/Yb ratios (4.65 and 2.19 in the basalt No. 5 and the dolomite No. 6, respectively) are slightly lower and higher than other basalts (5.95–9.47) and the dolomites (1.36–1.79), respectively. Therefore, slight mobilization of REE between the basalt and the dolomite is inferred, but is limited to the dolomite–basalt interface.

5.1.2. Dolomitization

According to Veizer et al. (1989b), most Archean carbonates in vugs of pillow basalts were originally deposited as calcite and converted to dolomite by secondary alteration. How dolomitization affects the intrinsic REE signatures of the carbonate deserves discussion before describing the possible preservation of the REE signature of the ancient seawater.

Quantitative modeling by Banner et al. (1988) indicates that large fluid-rock ratios (>10^4) are required to alter REE patterns in carbonates, because REE concentrations in carbonate rocks are generally 10^2–10^6 times higher than those in natural waters, such as groundwater and seawater. Therefore, dolomitization does not necessarily modify the original REE signatures of limestone (Banner et al., 1988; Qing and Mountjoy, 1994).

Since our dolomite samples show signs of hydrothermal alteration, hydrothermal water is another candidate for the dolomitizing solution. In this case, REE compositions of carbonate samples may be overprinted by hydrothermal REE, since hydrothermal solutions have 10^2–10^3 higher LREE concentrations than seawater (e.g. Douville et al., 1999). If the dolomite samples inherited REE signature of hydrothermal solution, they would be expected to show positive Eu anomalies because those solutions usually show such conspicuous anomalies (Klinkhammer et al., 1994). However, we find only weak Eu anomalies in the REE patterns of dolomites. Therefore the contribution of hydrothermal REE to dolomite samples seems, if any, not to be significant.

5.2. REE fractionation between seawater and carbonate

We have shown that the REE compositions of the dolomites have been affected by secondary processes to a limited extent. In order to estimate REE composition of ancient seawater from dolomite, it is important to have accurate REE partition coefficients between carbonate minerals (calcite/dolomite) and seawater. Despite many attempts to determine partition coefficients of REE between calcite and seawater by precipitation experiments and analyses of natural samples (Parekh et al., 1977; Scherer and Seitz, 1980; Terakado and Masuda, 1988; Zhong and Mucci, 1995), there are many discrepancies among the available datasets (Fig. 11 in Zhong and Mucci, 1995). This is probably due to the difference in experimental conditions and the diversity of the environments under which calcite was precipitated (Zhong and Mucci, 1995).

According to the experimental study by Zhong and Mucci (1995), LREEs are preferentially concentrated into calcite; the partition coefficients decreasing from 10^{3.6} (La) to 10^{1.9} (Yb), when the absolute individual concentration in reacting solution was maintained at 70 nM. The REE pattern of JDo-1 (dolomite reference sample issued by GSJ) normalized to seawater also shows smooth LREE enrichment without the tetravalent effect, although JDo-1 and seawater themselves show the apparent tetravalent effect in their respective chondrite-normalized REE patterns (Kawabe et al., 1998). Such a fairly smooth pattern can be explained by the similar bonding and coordination states of REE^{3+} ions in dolomite and REE^{3+}-carbonate complexes in seawater (Kawabe et al., 1998), suggesting that the partition coefficient between dolomite and seawater can be inferred from the analyses of JDo-1.

In Table 4, REE compositions of JDo-1 with different digestion methods are shown. Analytical data with the 1.7N HCl digestion are slightly lower than those by 6N HCl and subsequent HF + HClO₄ digests, suggesting the existence of 1.7N HCl insoluble components in JDo-1. Values by Kawabe et al. (1998) analyzed after 6.0N HCl digestions are systematically higher than our data by about 1–5%. This difference is likely to be ascribed to the difference in the analytical methods.

Based on our analyses on JDo-1 with 1.7N HCl digestion we calculated the partition coefficients between JDo-1 and seawater. The partition coefficients are defined as the ratio of (X_{REE}/X_{Ca})_{JDo-1}/([REE]/[Ca]_{seawater}, where X represents molar fraction (Zhong and Mucci, 1995). Normalization by [Ca] in seawater was necessary, because Zhong and Mucci (1995) reported that carbonate–seawater partition co-
Table 4

Analyses of JDo-1 (Dolomite standard sample of Geological Survey of Japan) and calculated partition coefficients of REE between the JDo-1 and the present shallow seawater

<table>
<thead>
<tr>
<th>Element</th>
<th>JDo-1 (ppm)</th>
<th>JDo-1 (ppm)</th>
<th>JDo-1 (ppm)</th>
<th>Shallow seawater (pmol/kg)</th>
<th>log D</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>7.56 ± 0.06</td>
<td>7.39 ± 0.06</td>
<td>7.91</td>
<td>25.7</td>
<td>3.55</td>
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<tr>
<td>Ce</td>
<td>2.06 ± 0.03</td>
<td>1.99 ± 0.02</td>
<td>2.16</td>
<td>5.66</td>
<td>3.66</td>
</tr>
<tr>
<td>Pr</td>
<td>0.966 ± 0.005</td>
<td>0.969 ± 0.002</td>
<td>0.99</td>
<td>3.62</td>
<td>3.51</td>
</tr>
<tr>
<td>Nd</td>
<td>4.21 ± 0.02</td>
<td>4.14 ± 0.02</td>
<td>4.25</td>
<td>16.2</td>
<td>3.48</td>
</tr>
<tr>
<td>Sm</td>
<td>0.686 ± 0.008</td>
<td>0.67 ± 0.004</td>
<td>0.706</td>
<td>3.04</td>
<td>3.40</td>
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<tr>
<td>Eu</td>
<td>0.154 ± 0.003</td>
<td>0.15 ± 0.001</td>
<td>0.16</td>
<td>0.811</td>
<td>3.32</td>
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<tr>
<td>Gd</td>
<td>0.872 ± 0.002</td>
<td>0.863 ± 0.006</td>
<td>0.91</td>
<td>4.49</td>
<td>3.32</td>
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<tr>
<td>Tb</td>
<td>0.113 ± 0.003</td>
<td>0.111 ± 0.002</td>
<td>0.128</td>
<td>0.724</td>
<td>3.21</td>
</tr>
<tr>
<td>Dy</td>
<td>0.747 ± 0.005</td>
<td>0.736 ± 0.01</td>
<td>0.774</td>
<td>5.29</td>
<td>3.16</td>
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<tr>
<td>Ho</td>
<td>0.164 ± 0.003</td>
<td>0.161 ± 0.001</td>
<td>0.176</td>
<td>1.53</td>
<td>3.03</td>
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<tr>
<td>Er</td>
<td>0.462 ± 0.003</td>
<td>0.453 ± 0.006</td>
<td>0.469</td>
<td>4.95</td>
<td>2.97</td>
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<tr>
<td>Tm</td>
<td>0.055 ± 0.001</td>
<td>0.054 ± 0.001</td>
<td>0.056</td>
<td>0.708</td>
<td>2.88</td>
</tr>
<tr>
<td>Yb</td>
<td>0.303 ± 0.003</td>
<td>0.297 ± 0.004</td>
<td>0.310</td>
<td>4.73</td>
<td>2.79</td>
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<tr>
<td>Lu</td>
<td>0.042 ± 0.001</td>
<td>0.040 ± 0.001</td>
<td>0.044</td>
<td>0.977</td>
<td>2.64</td>
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<tr>
<td>Ca</td>
<td>33.98</td>
<td>33.98</td>
<td>33.98</td>
<td>0.0103</td>
<td></td>
</tr>
</tbody>
</table>

a Average and standard deviation of three replicates; sample was digested with 6N HCl and subsequent concentration HF + HClO4 (2:1 in volume ratio).
b Average and standard deviation of three replicates; sample was digested with 1.7N HCl under heating less than 60°C.
c After Kawabe et al. (1998).
d For calculation of partition coefficients, JDo-1 values after 1.7N HCl digestion was used. The reason is stated in the text.
e Ca concentration of JDo-1 is expressed in %, and that of seawater in mol/l.

The partition coefficients of REEs are affected by [REE] : [Ca2+] ratios in solution. They also argued that possible effects of significantly higher PCO2 at 3.5 Ga than the present time (~0.07 atm at 3.5 Ga ago as estimated by the Owen’s scheme; Masonneuve, 1982) on REE partition coefficients are minimal. Therefore, we can safely ignore the effect of high PCO2 in our estimation of REE partition coefficients. Calculated partition coefficients are shown in Table 4 and are surprisingly consistent with those of Zhong and Mucci (1995) for LREE.

5.3. Estimated REE composition of 3.4 Ga seawater

Using our estimated partition coefficients of REE between dolomite and seawater (Table 4) and REE abundances in the Precambrian dolomites from our sample set, we calculated the REE composition of 3.4 Ga seawater (Fig. 6). For the calculation, two seawater Ca concentration values were used; 10.3 mmol/l as in the present seawater, and 232 mmol/l for 3.2 Ga seawater (De Ronde et al., 1997) estimated from the chemistry of fluid inclusions. We also plot the REE compositions of modern shallow and deep seawater (Kawabe et al., 1998) for comparison in Fig. 6.

As shown in Fig. 6, absolute abundances of REE in the 3.4 Ga hypothetical seawater depend strongly on the Ca concentration in the seawater, because absolute values of partition coefficients are primarily a...
function of Ca contents in seawater. When Ca concentration of present seawater is used for the calculation, LREE concentrations of 3.4 Ga seawater are comparable to those of present seawater. If the estimation of Ca concentration of 3.2 Ga seawater by De Ronde et al. (1997) is applied, REE concentrations of ancient seawater appear to be elevated with respect to present seawater.

In Fig. 6, the estimated REE pattern of 3.4 Ga seawater is characterized by a distinct HREE enrichment with respect to the chondritic composition. It should be noted that slight negative Ce anomaly is an artifact of the calculation owing to the difference in the degree of Ce anomaly between JDo-1 and present seawater. There also seems to be a positive Eu anomaly in 3.4 Ga seawater, most likely due to the addition of a hydrothermal component. Because hydrothermal waters are expected to have LREE-enriched patterns without tetrads – as observed in mid-ocean ridge hydrothermal vents – a less pronounced occurrence of a W-shaped tetrads effect in 3.5 Ga seawater is also consistent with the notion that it was affected by hydrothermal input.

Another important point is that the inferred degree of HREE enrichment in 3.4 Ga seawater is apparently larger than for the present seawater. This is consistent with REE studies on worldwide BIF that HREE enrichment was much more pronounced during early Precambrian than it is today (Bau and Möller, 1993). However, it is not clear which speciation of REE controls their concentrations in the hydrosphere and which anionic species or complexes may be important (Lewis et al., 1998). In general, REE speciation in natural waters is controlled by temperature, pH, salinity, and relative abundances of suitable ligands such as halides, sulfate, phosphate, carbonate and hydroxide (Wood, 1990a, 1990b). Kempe and Kazmierczak (1990) postulated based on comparison of seawater with the chemistry of modern alkaline lakes, that higher alkalinity and pH of the Early Precambrian seawater played an important role in generating the HREE-enriched water. Bau and Möller (1993) raised two further possibilities to account for the observed HREE patterns: (1) higher [CO$_3^{2-}$] in river and coastal waters, and (2) widespread REE redox-cycling at the interface between anoxic and oxic oceanic water masses. They concluded that these processes are synergic and could have operated concurrently. In waters from Lake Van, high pH and [CO$_3^{2-}$] generated conspicuous HREE enrichment in the REE pattern, with (Sm/Yb)$_n$ ratios as low as 0.05 (Möller and Bau, 1993). Additional REE studies of Precambrian carbonates could enhance our knowledge of the REE composition of concerned seawater, and the methodology described here could be a powerful tool for decoding the REE signatures of the ancient seawater.

6. Conclusions

Major and trace elemental analyses on dolomite samples intercalated in basaltic pillows from the Pilbara Block, Australia, were undertaken in order to examine the possibility of utilizing the carbonates to decipher the geochemical signatures of ancient seawater. The results lead to the following major conclusions:

1. All dolomite samples in this study show a downward convex tetrads effect in their CI-normalized REE patterns, strongly implicating the possible preservation of ancient seawater-related signatures in the dolomites. We note that such tetrads effects are absent if we apply the standard NASC- or PAAS-normalization. As shown in Fig. 7, Precambrian carbonates reported to date exhibit clear W-
type tetrad effects, an intrinsic characteristic of seawater from the early Archean to the present.

(2) Partition coefficients of REE were calculated between carbonate–seawater based on the analyses on the dolomite standard sample (JDo-1) after digestion by 1.7N HCl. Our estimates are consistent with those of Zhong and Mucci (1995), especially for LREEs. Given these partition coefficients and reported Ca contents of 232 mmol/l for 3.2 Ga seawater (De Rond et al., 1997), REE concentrations of ancient seawater could have been one to two orders of magnitude higher than those in the present-day seawater.

(3) Derived REE patterns for 3.4 Ga seawater show HREE enrichment and less pronounced W-type tetrad effect relative to that of present seawater. The latter can partly be attributed to the contribution from a hydrothermal fluid (with no tetrad effect), suggested by the slight positive Eu anomaly REE pattern of the proposed 3.5 Ga seawater. HREE enrichment in Archean seawater may be a result of higher [CO3$^{2-}$] in coastal waters combined with a widespread redox-cycling of the REE at the interface between anoxic and oxic oceanic water masses (Bau and Moller, 1993).

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