A refined dissolution method for rare earth element studies of bulk carbonate rocks

Kan Zhang, Xiang-Kun Zhu *, Bin Yan

Laboratory of Isotope Geology, MLR, State Key Laboratory of Continental Dynamics, Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China

ABSTRACT

Extraction of primary geochemical signals from bulk carbonate rocks is a key task in palaeoenvironmental studies. REE behaviour is investigated during stepwise dissolution of carbonate rocks. The experiment is designed to achieve total carbonate dissolution in ten steps, aiming for approximately 10% of the total carbonate to be dissolved in each step using acetic acid. An additional eleventh step using excess acid completed each experiment. Results show that calcite is preferentially dissolved before dolomite though no significant effect on the REE pattern of the rock is observed. Secondary carbonate phases and adsorbates are likely to be dissolved at the beginning of the dissolution process but this does not increase REE concentration though the REE pattern may be altered e.g. lessening of negative Ce anomaly, altering of Eu anomaly, Y/Ho ratio and relative fractionation between LREE and HREE. Non-carbonate minerals e.g. terrestrial particulate matter, Fe–Mn oxyhydroxides and phosphates, are likely to be dissolved towards the end of the total dissolution, especially in the final excess acid step. This should increase REE concentrations and alter REE distribution patterns greatly. In contrast, solutions from intermediate steps are less contaminated. Further, compared with using 10% v/v acetic acid, the solutions obtained using 5%v/v acid return more pristine REE information from the carbonate.

A proposed method for REE studies of bulk carbonate rocks requires an initial dissolution of 30%–40% followed by the sampling dissolution of 30%–40% of total carbonate using 5%v/v acetic acid to produce REE information considered to best represent that of the carbonate source water. Following these steps 20%–30% of the carbonate should remain undissolved, thus minimising contamination from non-carbonate minerals.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The rare earth element (REE, including yttrium) geochemistry of authigenic carbonates has shown itself to be an important tool for studying the water from which they precipitated (Webb and Kamber, 2000; Nothdurft et al., 2004; Shields and Webb, 2004; Ge et al., 2010; Delpomdor et al., 2013). Similar ionic radii and the predominance of trivalent valence states make the lanthanide series (including Y) act as a coherent group during geological and geochemical processes. However, small but systematic differences in the properties of REE make it possible to use them to constrain depositional environments of ancient carbonate rocks (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Bolhar et al., 2004; Nothdurft et al., 2004; Bolhar and Van Kranendonk, 2007; Pourret et al., 2007; Frimmel, 2009; Rongemaille et al., 2011). For example, the Ce anomaly can be used as a redox tracer. Redox-sensitive Ce exists in either trivalent or tetravalent form, and soluble Ce^{3+} can be oxidized to highly insoluble Ce^{4+} in oxygenated water. Thus a negative Ce anomaly exists in oxygenated water and the carbonate rocks precipitated from it; correspondingly, a positive Ce anomaly exists in Fe–Mn

sediments where the tetravalent Ce ion is prone to be adsorbed (Elderfield et al., 1981; Elderfield and Sholkovitz, 1987; Bau et al., 1996; Slack et al., 2007; Birgel et al., 2011; Ling et al., 2013; Loope et al., 2013). Eu^{3+} can be reduced to Eu^{2+} under extremely reducing conditions. However, a Eu anomaly in seawater may not reflect the redox state of water, but is generally regarded as an indicator of hydro-thermal input (Derry and Jacobsen, 1990; Danielson et al., 1992; Wheat et al., 2002; Bolhar and Van Kranendonk, 2007; Frimmel, 2009; Wang et al., 2014). The Y/Ho ratio can serve as a monitor for differentiating between different water types (Nozaki et al., 1997; Wang et al., 2014). Seawater has a higher Y/Ho ratio than freshwater, and the elevated Y/Ho ratio results from Ho being scavenged two times faster than Y from the surface ocean to the deep ocean because of different surface complexing behaviour (Nozaki et al., 1997). Generally, the PAAS-normalized REE distribution patterns of typical marine carbonates are similar to modern seawater which is characterized by an enrichment of HREE, a positive La anomaly (~2.62 in average), negative Ce anomaly (in oxygenated condition), subtle positive Gd anomaly and a super-chondritic Y/Ho ratio (44–74) (Bau et al., 1996; Zhang and Nozaki, 1996; Bolhar et al., 2004; Shields and Webb, 2004; Lawrence et al., 2006). By contrast, freshwater carbonates display slight LREE depletion or enrichment, or MREE enrichment, no distinct element anomalies, and

* Corresponding author.
  E-mail address: xiangkun@cags.ac.cn (X.-K. Zhu).

near-chondritic Y/Ho ratios (Sholkovitz et al., 1999; Lawrence et al., 2006; García et al., 2007).

When using REE for palaeoenvironmental studies, it is crucial to ensure that the information extracted from bulk carbonate rocks is not affected by diagenetic alteration or contaminated by non-carbonate materials. Although diagenetic fluids are generally considered to have little effect on the primitive REE features in carbonate rocks due to their low REE concentrations (Banner et al., 1988; Sholkovitz et al., 1989; Banner and Hanson, 1990; Webb and Kamber, 2000; Lin et al., 2011), this does not mean their influences can be entirely ignored (Shields and Stille, 2001; Bolhar and Van Kranendonk, 2007; Ling et al., 2013). Moreover, possible contamination from non-carbonate minerals, such as terrestrial particulate matter, Fe–Mn oxyhydroxides and phosphates, can never be dismissed (Elderfield, 1986; Elderfield et al., 1990; Bau et al., 1996; Nothdurft et al., 2004). To deal with these potential problems, various partial dissolution methods have been proposed. For examples, in the study of Nothdurft et al. (2004), the carbonates for REE determination were obtained through dissolving samples in ultra-pure 1 M acetic acid; in the study of Zhao et al. (2009), samples were dissolved in 0.5 M acetic acid at room temperature for 4 h; in the study of Rongemaille et al. (2011), the use of 5%v/v acetic acid at room temperature with duration of 24 h is recommended. However, no systematic investigation on the REE behaviour during dissolution of carbonate rocks has been conducted in previous studies. This leaves some uncertainty over the accuracy of the proposed dissolution methods.

Detailed stepwise dissolution experiments, for example in the study of strontium isotope stratigraphy (SIS) by Bailey et al. (2000), may well separate REE signals from different components in bulk carbonate rocks, including different carbonate phases and non-carbonate materials. Thus the genuine signature reflecting the water-column from which the carbonates precipitated may be recovered or obscured depending on the dissolution process. This paper reports the results of such experiments, and accordingly proposes a refined dissolution method for the REE study of bulk carbonate rocks.

2. Materials and methods

2.1. Experimental design

In the stepwise dissolution experiments, about 10% of total sample carbonate is designed to be dissolved in each step, thus requiring ten steps. This is followed by an eleventh step during which sample residue is treated with excess dilute acetic acid. Previous studies indicate that dilute acetic acid can minimise the contamination from non-carbonate minerals while dissolving calcite and dolomite (Bailey et al., 2000; Zhao et al., 2009; Li et al., 2011; Rongemaille et al., 2011). To investigate the effect of acid strength, 5%v/v (0.86 M) and 10%v/v (1.73 M) acetic acid are used for comparison. Samples of different types of carbonate rocks are selected for investigation.

2.2. Samples

A limestone, a calcareous dolostone, a siliceous dolostone and a pure dolostone were prepared for the stepwise dissolution experiments.

Sample L refers to a limestone collected from the third Member of Mesoproterozoic Gaoyuzhuang Formation in Jixian Section, North China. It contains 46.38% CaO and 5.56% MgO, and the contents of SiO_2, Al_2O_3 and TFe_2O_3 are 6.13%, 0.24% and 0.14%, respectively.

Sample CD refers to a calcareous dolostone collected from Neoproterozoic Doushantuo cap carbonate in Tianjiayuanzi Section, South China. It contains 31.55% CaO and 13.33% MgO, and the contents of SiO_2, Al_2O_3 and TFe_2O_3 are 10.21%, 2.56% and 1.40%, respectively.

Sample SD is a siliceous dolostone collected from Neoproterozoic Doushantuo cap carbonate in Jiulongwan Section, South China. It contains 15.84% CaO and 10.57% MgO, and the contents of SiO_2, Al_2O_3 and TFe_2O_3 are 39.92%, 3.91% and 2.75%, respectively.

Sample D is the powdered dolostone standard SRM 88b purchased from the National Institute of Standards and Technology (NIST), U.S. It contains 29.95% CaO and 21.03% MgO, and the contents of SiO_2, Al_2O_3 and TFe_2O_3 are 1.13%, 0.336% and 0.277%, respectively.

Concentrations of Ca, Mg, Si, Al, and Fe of the first three samples were analysed with an X-ray fluorescence spectrometer in the National Research Center for Geoanalysis, China, while those of Sample D were obtained from the NIST material database.

For Sample L, the powders used for experiments were obtained by micro-drilling on a fresh surface of a rock slab; whereas Samples CD and SD were first broken into small pieces, and clean fragments were then selected and pulverized in an agate mortar. For both physical extraction methods, efforts were made to avoid veins, later-stage cements, etc.

2.3. Experimental procedure

All experiments were carried out in a class 100 ultra-clean laboratory in the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences. Acids used in the study were purified using DST-1000 device from American Savillex company, and 18.2 MΩ-cm ultrapure water was prepared by PURELAB® ultra water system from British Elga company. All containers and pipette tips used were cleaned thoroughly following strict procedures.

Sample powders (~0.6 g) were weighed in 50 ml polypropylene centrifuge tubes, and two sets of materials were prepared for dissolution using 5%v/v and 10%v/v acetic acid respectively. The volumes of dilute acetic acid used in each steps were calculated to dissolve 10% of carbonate, the content in each sample being estimated from its total CaO and MgO. The calculated volume of acetic acid was added into samples in their centrifuge tubes, then the tubes were sonicated intermittently in an ultrasonic bath. The reaction time was fixed at 24 h, ensuring a complete reaction (no more bubble generation). The leachates were obtained by centrifuging, while the residue was rinsed three times using ultrapure water. The water was then added to the previous supernatant. This partial dissolution procedure was repeated another 9 times, and a total of 10 leachates were obtained from each tube. Finally, excess 5%v/v or 10%v/v acetic acid (about 5 times of the previous volume) was added into each tube to get the eleventh leachate. After the entire stepwise extraction, all the leachates were converted to nitric acid medium, and an aliquot of each leachate was then taken for elemental analysis.

The elemental analysis was carried out at the State Key Laboratory for Mineral Deposits Research, Nanjing University. There, the dried aliquots were dissolved in 5 ml 3% HNO_3, and 100 μl Rh (200 ppb) was added in each sample as an internal standard for correcting matrix effects and instrument drift. The trace elements were determined using a Finnigan MAT ELEMENT 2 ICP-MS, and the major elements were measured by ICP-AES of JY3S, with analytical precisions better than 5% and 2% respectively. Some samples were diluted 20-fold again for Ca or Mg determination.

3. Results

The data are not included in this publication but are available in the online Appendix, their main features are described in the following text.

3.1. Ca and Mg

Variations in the amount of Ca + Mg released during the stepwise dissolution process are shown in Fig. 1a. Among the first nine or ten steps, the Ca + Mg released in each step is approximately 10% of the total Ca + Mg in each sample, and becomes much lower in step 11. For Sample L, the amount declines in step 10, especially for the series treated with 10%v/v acetic acid. These results indicate that the carbonate content in the samples has been almost totally consumed during the first ten steps as expected. Variations in the Mg/Ca molar ratio