



Organic matter removal for the analysis of carbon and oxygen isotope compositions of siderite



Oanez Lebeau*, Vincent Busigny, Carine Chaduteau, Magali Ader

Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France

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ABSTRACT

The measurement of stable carbon (C) and oxygen (O) isotope compositions in siderite from sediments and soils can be useful to constrain carbonate genesis processes and/or to reconstruct paleoclimates. In order to evaluate our ability to determine C and O isotope compositions of siderite in modern sediments and soils containing immature organic matter, we prepared and analyzed synthetic samples made of variable proportions of pure siderite and yeast (selected for representing an immature organic matter because of its potential high reactivity to H_3PO_4 digestion). Replicate analyses of CO_2 produced by phosphoric acid (H_3PO_4) digestion of our pure siderite standard at 130 °C provided $\delta^{13}\text{C}_{\text{sid}}$ and $\delta^{18}\text{O}_{\text{sid}}$ values of $-12.3 \pm 0.1\%$ and $-16.2 \pm 0.3\%$ (2σ) relative to PDB. Analysis of the synthetic sample mixtures shows $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values undistinguishable from those of pure siderite within uncertainties, for proportion of yeast in the mixture equal to or lower than 10 wt.% (corresponding to ~5 wt.% of total organic carbon). In contrast, samples with proportions of yeast higher than 10 wt.% were progressively shifted to more negative values (down to -21.8% for C and -19.6% for O) with increasing proportion of yeast, as a result of an increasing contribution of CO_2 produced by the reaction of yeast with H_3PO_4 at 130 °C. Although in the case of natural samples this organic matter CO_2 contribution probably strongly depends on both organic matter source organisms and diagenetic history, our data indicate that the removal of organic matter prior to siderite analysis may be often required. We thus tested three different methods for organic matter removal on our synthetic samples, using either oxidation in solution with NaOCl or H_2O_2 , or oxidation in low-temperature oxygen-plasma ashing system. For both methods based on oxidation in aqueous solution, we show that the determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is improved for concentration of yeast lower than 75 wt.% in the "siderite–yeast" mixture but is still shifted to lower values by 4.1 and 0.7‰ for C and O respectively, for a yeast proportion higher than 75 wt.%. Moreover, these two methods induce partial siderite dissolution, preventing determination of siderite content in the samples. The best method of yeast removal for coupled C and O isotopes analysis is the oxidation by low-temperature oxygen-plasma ashing, which strongly improves the accuracy of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements and perfectly preserves siderite. In conclusion, any study of siderite isotope composition in organic-rich samples should include an evaluation of the need for organic matter removal using low-temperature oxygen-plasma ashing, the only method shown here to be efficient while preserving the siderite.

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1. Introduction

Siderite (FeCO_3) in sediments and soils is an authigenic carbonate, formed under reducing conditions from ferrous iron (Fe^{2+}) and carbonate ions dissolved in porewaters. Dissolved Fe^{2+} can accumulate to significant level only in the absence of molecular oxygen (O_2) and hydrogen sulfide (H_2S) because Fe^{2+} is oxidized to Fe^{3+} and forms iron oxyhydroxides in the presence of O_2 , and reacts to produce iron sulfide in the presence of H_2S (see review in Coleman, 1985). Siderite is thus mostly found in settings characterized by high organic matter burial rates (driving O_2 exhaustion and iron oxides reduction) and low sulfate (SO_4) content (limiting H_2S production by sulfate reduction).

These conditions are mostly encountered in modern continental depositional settings such as soils (Ludvigson et al., 1998; McMillan and Schwertmann, 1998; Ratering and Schnell, 2000; Rakshit et al., 2008; Driese et al., 2010), bogs (Postma, 1981) and lakes (Emerson, 1976; Bahrig, 1989; Sapota et al., 2006; Schettler et al., 2007). They can also be found in marine sediments, in which O_2 and SO_4 diffusion from seawater is limited by the sediments low permeability, leaving iron reduction and methanogenesis as the main mechanisms for organic matter degradation (Matsumoto, 1989; Chow et al. 2000; Pierre et al., 2000). In ancient Fe-rich sedimentary deposits such as Banded Iron Formations, siderite can be a major phase and is usually interpreted as resulting from organic matter degradation by iron reduction in sediments overlain by sulfate-poor and ferruginous water column (James, 1954; Perry and Tan, 1972; Hangari et al., 1980; Maynard, 1982; Thyne and Gwinn, 1994; Fisher et al., 1998; Busigny et al., 2013).

* Corresponding author.

E-mail address: olebeau@ipgp.fr (O. Lebeau).

Carbon and oxygen isotope compositions of sedimentary siderite can potentially be used to decipher its conditions of formation, and to test whether it involved biotic or abiotic processes. The carbon isotope composition of siderite records the signature of dissolved inorganic carbon from which siderite precipitates, similarly to other carbonates (Zhang et al., 2001). It therefore allows identification of the major biogeochemical zone in which siderite has precipitated and the involvement of specific metabolisms (anaerobic respiration or methanogenesis) in the establishment of favorable conditions for its formation (Irwin et al., 1977; Curtis et al., 1986; Moore et al., 1992; Mozley and Burns, 1993; Pierre et al., 2000). The O isotope composition of siderite primarily depends on the precipitation temperature and the porewater $\delta^{18}\text{O}$ value (Zhang et al., 2001), thus providing information on the diagenetic temperature and the origin of diagenetic fluids (Mozley and Burns, 1993; Wilkinson et al., 2000). However, microbially-induced precipitation of siderite may significantly modify O isotope fractionation compared to abiotic processes (e.g. Mortimer and Coleman, 1997), complicating the use of $\delta^{18}\text{O}$ as a tracer of diagenetic temperature and fluid. Studies of siderite formation in modern systems, for which temperature, porewater $\delta^{18}\text{O}$ and microbial activity can be characterized, are thus required to unambiguously constrain the processes controlling siderite $\delta^{18}\text{O}$. However, before performing such studies, it is necessary to develop a robust method for measuring C and O isotope compositions of siderite present in minor amounts in sediments rich in immature organic matter. While several authors focused on the analysis of organic C isotope composition in carbonate-rich samples (France-Lanord and Derry, 1994, 1997; Galy et al., 2007; Brodie et al., 2011a,b), the C and O isotopes analysis of carbonates in organic-rich matrix remains poorly constrained, particularly for siderite. Yet, the presence of organic matter associated with carbonates has long been suspected to offset the measurement of C and O isotope compositions of calcite and aragonite, so that various treatments aiming at removing organic matter have been tested (e.g. Wierzbowski, 2007; Fallet et al., 2009). The interference of organic matter on carbonate analysis is generally interpreted as due to CO_2 and/or other molecular gaseous species production during the reaction of organic matter with phosphoric acid (H_3PO_4) used for carbonate dissolution (Epstein et al., 1951, 1953; Bowen, 1966; Weber et al., 1976) and incomplete separation of these gases during vacuum purification. To our knowledge, no treatments have been established for non-traditional carbonates like siderite (FeCO_3) or magnesite (MgCO_3). Yet, the effects associated with the presence of organic matter in these samples are expected to be even more important because of the high reaction temperature required for siderite dissolution using H_3PO_4 (~130 °C; Rosenbaum and Sheppard, 1986). Moreover most of the treatments have been tested for off-line CO_2 extraction and purification in a vacuum line while most laboratories now use on-line methods with a gas chromatographic column separation, which may be more efficient to separate CO_2 from other contaminant gaseous species. In this paper we fill this gap for siderite analysis using a GC–IRMS technique, separating contaminant gases from CO_2 before C and O isotope measurements in the mass spectrometer.

We tested several procedures to remove organic matter from a synthetic siderite–organic mixture before siderite analysis. Synthetic samples were prepared by mixing pure siderite with various proportions of yeast, a living microorganism taken here as a model for the most immature organic material. We expected high reactivity to H_3PO_4 digestion at 130 °C, with potentially extreme C and O isotope effects, thus placing an upper limit for C and O isotope offsets expected in natural samples. Indeed, carbon and oxygen isotope analyses of the siderite using H_3PO_4 digestion (McCrea, 1950) and GC–IRMS isotope analyses (Assayag et al., 2006) are shown to be affected by the presence of yeast in the sample.

In order to improve siderite C and O isotope analysis, three organic matter oxidation treatments were tested: two involved wet chemistry (using NaOCl or H_2O_2) and one low-temperature oxygen-plasma ashing (Goreau, 1977). Roasting in vacuum or helium at 300 to 400 °C, a

commonly used treatment to remove organic matter from carbonates (e.g., Epstein et al., 1951, 1953; Wierzbowski, 2007), was not considered here because siderite destabilization starts at ~300 °C (Froelich, 1980).

2. Experimental technique

2.1. Preparation of the experimental material

In the present work, pure yeast (*Saccharomyces cerevisia*) was selected to represent an organic matter because it is highly immature and probably most reactive to H_3PO_4 . Additionally, yeast presents two main advantages: (1) it can be easily purchased and is inexpensive, and (2) it can be well preserved under dried and cooled conditions without any evolution of its C isotope composition. The yeast was purchased at “L’atelier de la pâtisserie” (labeled LEVURE-SECHE) in 500 g box as dry balls of 1 mm of diameter. It was ground, sieved to fraction of <150 μm and homogenized.

After examination under binocular microscope, Raman spectroscopy and electron microprobe, siderite from the deposit of La Mûre (France) was selected for our experiments. This siderite contains mostly Fe (90.0 ± 2.0%), with minor amount of Mg (5.0 ± 1.0%), Mn (2.4 ± 0.3%) and Ca (1.1 ± 0.2%) and does not show evidence of alteration to Fe-oxides. Siderite crystals were crushed to small fragments (<500 μm), before being carefully selected under a binocular microscope. Suspicious “colored” fragments were discarded to avoid any potential contamination with other minerals (e.g. traces of alteration, Fe oxides, or mineral inclusions). The pure fraction was then ground to <100 μm using an agate mortar and homogenized. All grains smaller than 100 μm were used, including very fine-grained material. This siderite powder was labeled SID.

Finally, nine synthetic samples were prepared with variable proportions of yeast and siderite ranging from 0 to 100 wt.% yeast (see Table 1), and were homogenized by shaking.

2.2. Methods for organic matter removal

For the chemical treatments, about 150 mg of the nine synthetic samples were weighed and introduced into clean glass beakers. A large excess (30 to 40 ml) of oxidizing solution, either NaOCl 3.5% or H_2O_2 30%, was added to the powders and left at room temperature (~22 °C) during 3 days with regular shaking of the solution (adapted from Wierzbowski, 2007). The powders were then rinsed several times ($n = 6$) with deionized water and dried in an oven at 50 °C during 3 days.

The third method, tested in the present work, was low-temperature oxygen-plasma ashing in a POLARON PT7160 RF system. For the experiment, 35 to 320 mg of the samples were weighted and loaded in a petri dish. The petri dish was covered with riddled alumina foil and introduced in the vacuum chamber of the plasma ashing system. After evacuation of the air contained in the chamber, oxygen was injected and an electric discharge lit the plasma. The oxygen plasma is made of free radicals, which oxidize the organic matter to CO_2 . The reaction time was comprised between 300 and 1860 min depending on the amount of yeast in the sample.

2.3. Carbon and oxygen isotope analyses

Carbon and oxygen isotope compositions of our pure siderite and synthetic mixture samples were determined using a modified McCrea method (McCrea, 1950) and a He continuous flow mass spectrometer (AP2003, Analytical Precision, UK). The procedure can be described as follow. Two to 50 mg of powders was loaded in exetainer tubes. The air contained in the tubes was flushed with a He flow at 2.5 bar via a Gilson autosampler and 400 μL of phosphoric acid were injected manually through the septa with a 10 ml syringe. The temperature used for siderite reaction with phosphoric acid (H_3PO_4) was determined from

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