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Siderite acid fractionation factors for sealed and open vessel digestions at 70 °C and 100 °C

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ABSTRACT

The oxygen isotope composition of siderites can be used to deduce the paleoenvironmental conditions under which the mineral formed. However, it is not clear whether the published fractionation factors ($\alpha_{\text{CO2-siderite}}$) for the acid digestion of siderites are appropriate for modern "on-line" sample preparation techniques. This is an important source of uncertainty that has not yet been investigated. To this aim, we obtained new siderite acid fractionation factors for open and closed vessel digestions at 100 °C and 70 °C, respectively. We find that previous $\alpha_{\text{CO2-siderite}}$ estimates are appropriate for GasBench-type sealed vessel digestions and propose a revised relationship between $\alpha_{\text{CO2-siderite}}$ and temperature:

$$1000\cdot\ \ln\left(\alpha_{\text{CO2-Siderite}}\right) = 4.06 \pm 0.17\ \left(10^3/T\right) - 1.93 \pm 0.5\ \left(R^2 = 0.99\right)$$

This relationship encompasses most practical laboratory digestion temperatures and has a temperature sensitivity of −0.032‰/°C that is similar to other carbonate minerals. The open vessel digestion $\alpha_{\text{CO2-siderite}}$ at 100 °C, on the other hand, is offset from previous estimates by 1‰, with a value of $1000\cdot ln\alpha = 9.79 \pm 0.23$ (0.12 SE). This estimate is essential for the open vessel digestions that are needed for siderite clumped isotope analyses.

1. Introduction

The oxygen (O) isotope composition of siderites can be exploited to reconstruct the environmental conditions of carbonate formation (Ludvigson et al., 1998; Ludvigson et al., 2013). For instance, siderite $\delta^{18}O$ values have been widely used as a proxy for the oxygen isotope composition of paleoprecipitation (White et al., 2001; Ufnar et al., 2002; Suarez et al., 2009), a useful paleoenvironmental variable that can be used to estimate ancient rainfall amounts (White et al., 2001; Poulsen et al., 2007; Suarez et al., 2011). Moreover, thanks to the recent development of the clumped isotope paleothermometer (Ghosh et al., 2006), the isotopic composition of siderites can be used directly to estimate temperatures of mineral formation (Fernandez et al., 2014). In spite of that, one source of uncertainty still to be investigated is the effect of incorrect O isotope phosphoric acid fractionation factors on the accuracy of siderite based paleoclimate reconstructions.

Carbonate samples have traditionally been measured for their stable O isotope composition after digestion with anhydrous phosphoric acid. The acid reaction, however, releases only 2/3 of the available O as CO_2 and results in an O isotope fractionation that is dependent on digestion temperatures, on carbonate mineralogy, and on sample digestion techniques (McCrea, 1950; Rosenbaum and Sheppard, 1986; Swart et al., 1991; Kim et al., 2007). Consequently, mineral and method specific acid fractionation factors ($\alpha_{\text{CO2-carbonate}}$) are needed to correctly estimate the $\delta^{18}O$ of solid samples.

Only two previous studies have attempted to estimate siderite acid fractionation factors. Rosenbaum and Sheppard (1986) determined the total oxygen isotope composition of synthetic and natural siderites using a combination of thermal decomposition and fluorination and reported $\alpha_{\text{CO2-siderite}}$ values at 100 °C and 150 °C. Likewise, Carothers et al. (1988) used similar methods to report $\alpha_{\text{CO2-siderite}}$ values at 25 °C and 50 °C. Both of these studies, however, utilized only a limited number of measurements for their total oxygen isotope determinations, so the uncertainties in their $\alpha_{\text{CO2-siderite}}$ values are not well constrained. More importantly, however, both studies used the "sealed vessel" acid digestion technique, which is based on the original McCrea (1950) method. With the advent of on-line sample preparation techniques this method is no longer routinely used, and it has not yet been shown whether the published "sealed vessel" $\alpha_{\text{CO2-siderite}}$ values are appropriate for modern sample preparation techniques.

Since the choice of incorrect siderite acid fractionation factors propagates directly into paleoclimate reconstructions, the lack of method specific $\alpha_{\text{CO2-siderite}}$ values represents an important yet often overlooked source of uncertainty. This is especially critical for siderites because there are no international standards with agreed upon $\delta^{18}O$ values.

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Here, we compare the $\delta^{18}O_{siderite}$ values that result from two common acid digestion techniques: 1) an "open vessel" method that is analogous to the on-line common acid bath carbonate digestion procedure, and 2) an on-line "sealed vessel" method where samples are digested with a GasBench II (Thermo Fisher Scientific) preparation device. We find a constant offset in the $\delta^{18}O_{siderite}$ estimates produced between both digestion styles and estimate new method specific $\alpha_{CO2\text{-}siderite}$ values.

2. Methods

2.1. Siderite samples

Four natural siderite samples were obtained from the museum collection at ETH Zurich to calculate $\alpha_{CO2\text{-}siderite}$ values. The samples were hand crushed with the aid of a mortar and pestle, passed through a 120 μm sieve, and stored in gas-tight Vacutainers. The mineralogy of the samples was confirmed with XRD analyses, which revealed that siderite was the only phase present in the samples. Chemical compositions were determined by ICP-MS analyses (Thermo Scientific Element XR) of homogenized sample aliquots (300 μg) after complete digestion by doubly distilled HNO_3. The Fe content in these samples ranges from 70 to 90%, with varying amounts of Ca and Mg (Fig. 1).

Additionally, five synthetic siderites were precipitated following the methods described in Wiesli et al. (2004) and Fernandez et al. (2014) and were used to compare the $\delta^{18}O_{siderite}$ obtained by both digestion methods. The mineralogy of these samples was also confirmed with XRD analyses prior to isotopic analyses.

2.2. Total oxygen isotope analyses

The isotope compositions of the total oxygen content of the siderite samples were determined with a high temperature pyrolysis system (TCEA) coupled to a continuous flow isotope-ratio mass spectrometer (CF-IRMS). Approximately 200 μg of carbonate was weighed into silver capsules along with 200 μg of graphite to provide excess carbon at the site of pyrolysis (Crowley et al., 2008). Samples and standards were loaded into a zero blank autosampler and dropped into a glassy carbon pyrolysis column held at 1450 °C and filled with glassy carbon chips. Samples were dropped into the furnace, and the resulting CO gas was transferred with the aid of a He carrier gas through a gas chromatography column into a Delta V Plus mass spectrometer for measurement (Thermo Fisher Scientific).

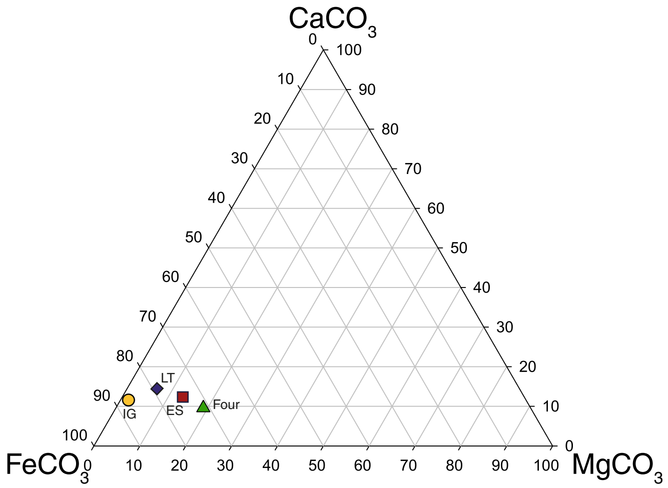

Fig. 1. Ternary diagram showing relative Ca, Fe, and Mg compositions of the four natural siderites used to estimate the siderite acid fractionation factor. Analytical uncertainty based on the analyses of multiple replicates is approximately 5% for Fe and 3% for Ca and Mg.

Three benzoic acid standards (IAEA 601, $\delta^{18}O_{VSMOW} = 23.3‰$; IAEA 602, $\delta^{18}O_{VSMOW} = 71.4‰$; B1-internal, $\delta^{18}O_{VSMOW} = 24.5‰$) and a cellulose standard (IAEA C3, $\delta^{18}O_{VSMOW} = 31.85‰$, Buhay et al., 1993) were used to calibrate measurements into the VSMOW scale and to correct for drift and linearity. The amount of CO produced during carbonate pyrolysis was calculated using the relationship between the weights of the three benzoic acid standards and their observed areas under the *m*/*z* 28 peaks, and yields were estimated using the expected amounts of CO based on sample stoichiometry.

2.3. Sealed vessel digestion

Sealed vessel digestions were performed in 12 ml exetainers loaded with approximately 200 μg of carbonate (siderite and calcite standards) and flushed with helium using the procedures outlined in Breitenbach and Bernasconi (2011). Reaction temperature was controlled using the aluminum block of the Gas Bench II (Thermo Fisher Scientific), which was held at 70 °C. After thermal equilibration, samples were injected with 5 drops (50 μl) of 100% phosphoric acid. In a subset of the experiments, reaction times were varied from 4 to 60 h to investigate the time necessary to fully digest the siderite samples. Reaction products were purified with a chromatography column, and the CO_2 was measured in continuous flow mode in a Delta V Plus mass spectrometer (Thermo Fisher Scientific) as described in Breitenbach and Bernasconi (2011). Two internal calcite standards were used to correct for drift and linearity. Digestion yields were calculated in a similar manner as the TCEA data, except that in this case the mass of the calcite standards and the area under the *m*/*z* 44 peak were used to build a calibration relationship.

2.4. Open vessel digestion

Open vessel digestions were performed at 100 °C in McCrea type reaction vessels attached to a vacuum line (see Fig. S1 in supplementary materials for an example of our setup). Approximately 15 mg of carbonate (standards and siderite samples) were loaded into the reactors, and the acid arm was filled with 1 ml of 104% phosphoric acid. Vessels were evacuated under vacuum and placed in a 100 °C boiling water bath. Enough time was allowed for thermal equilibration before tipping the acid from the side arm into the carbonate reservoir to start the reaction. As the reaction proceeded, the CO_2 was continuously trapped in a spiral trap cooled with liquid N_2. In most cases the reaction was allowed to proceed for up to 3 h; although, reaction times were varied in a separate set of experiments to investigate the optimal times for complete digestions.

Gasses were cleaned cryogenically in a vacuum line. Water was removed using two spiral water traps held at approximately −80 °C with an ethanol-liquid N_2 slush, and organic contaminants were removed by passing the gas through a U-shaped glass trap filled with a gas chromatography resin (Porapak Q) held at approximately −40 °C. The amounts of CO_2 produced were measured manometrically and digestion yields were estimated using sample stoichiometry. The clean gases were flame sealed into pre-combusted Pyrex tubes and measured in a MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific) operating in dual inlet mode.

2.5. Calculation of solid siderite $\delta^{18}O$ values

Two internal calcite standards were measured along with samples digested at 70 °C and four different standards were used with samples digested at 100 °C. The internal standards were first calibrated using the VSMOW-SLAP scale following International Union of Pure and Applied Chemistry (IUPAC) guidelines as described by Kim et al. (2015) through repeated measurements of NBS-19 and NBS-18. These standards were then used to calibrate siderite CO_2 gas into the VSMOW-SLAP scale and were corrected for acid fractionation following the