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Research paper

In-situ monitoring of the formation of carbon compounds during the dissolution of iron(II) carbonate (siderite)

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ABSTRACT

Experiments of dissolution of siderite ($FeCO_3$) in pure water and in saline aqueous solution ("seawater" composition) have been performed at temperatures of up to 400 °C in a maximum pressure range of 720–1150 MPa, using an hydrothermal diamond anvil cell (HDAC). The reaction products were characterized in situ by Raman spectroscopy. At 250 °C, in pure water system, we document formation of formaldehyde (HCOH) near the surface of siderite. At 250 °C and above, formic acid (HCOOH) and carbon monoxide (CO) were detected in the bulk fluid. The reduction of oxidized carbon to HCOH and HCOOH is coupled to conversion of ferrous iron (Fe^{II}) from siderite to ferric iron (Fe^{III}). We thus provide experimental evidence of Fe^{II}–CO_2 oxido-reductive coupling using a single mineral, siderite, in pure water and in saline solution. The presence of NaCl in the fluid enhances the kinetics of oxido-reductive dissolution of siderite, with formation of organic chlorinated molecules. The results suggest that in geological situations, especially in accretion prisms or active hydrothermal systems developing on ultrabasic rocks in which fluids may be transferred with relatively short residence times, formic acid and formaldehyde might be important metastable storage forms of hydrogen. Moreover, thermal dissolution of siderite may account for at least some of the reduced carbon observed in chondrites bearing traces of hydrothermal activity and in metasedimentary rocks from the early Earth.

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1. Introduction

Detailed studies of devolatilization reactions, fluid–rock interactions and metamorphic transformations occurring in the subducting slab play a key role in unraveling the complex physical–chemical transformations of crust and mantle at convergent margins and in the understanding of the fluid and element fluxes involved. One of the main characteristics of subduction zones is the presence of water or of hydrous fluids released from oceanic lithosphere that interact with mantle wedge rocks. In particular, reaction of water with ferrous iron-rich minerals contained in ultramafic rocks (such as olivine) can develop strongly reducing conditions and generation of H_2 during serpentinization (e.g. Sleep et al., 2004; Klein et al., 2009). For such reactions, $Fe^{(II)}$ carbonates can be considered as a good proxy for sedimentary materials. Siderite $FeCO_3$ either as an end-member or in solid solutions (e.g. in magnesite or ankerite) is a common constituent of low-grade sedimentary rocks and of hydrothermal vents on Earth and is present in accretion prisms in which it is an important iron source. Moreover, siderite has been identified in extraterrestrial materials such as meteorites (Romanek et al., 1994). This mineral is of particular interest because, as an iron carbonate, its stability is strongly dependent on pressure

(P), temperature (T) and on the fugacity of both CO_2 and O_2 (cf. French and Rosenberg, 1965; French, 1971; Koziol, 2004). Hence, siderite participates in reactions involving oxidation and reduction and provides information about the behavior of volatile components (H_2O, CO_2,…).

An experimental work by McCollom (2003) supports the possibility that thermal decomposition of siderite could provide a source for extra-terrestrial organic compounds, e.g. in Martian meteorites. Similar processes are invoked as a source of reduced carbon in metamorphic rocks from early Earth (Van Zuilen et al., 2002, 2003).

Despite these primary implications and the growing interest on solubility products and dissolution kinetics of siderite (Bénézeth et al., 2009; Testemale et al., 2009), laboratory experiments involving *in-situ* observations on decomposition of siderite have not been so far reported. Experimental studies of carbon compounds under hydrothermal conditions have been conducted using dissolved CO, CO_2, formic acid or methane as the main carbon source (Horita and Berndt, 1999; McCollom and Seewald, 2001, 2003; Seewald et al., 2006; McCollom et al., 2010). As far as the authors are aware, *in-situ* hydrothermal organic synthesis experiments using a single carbonate mineral as the carbon source have never been reported.

For a better understanding of these processes, H and C speciation can be monitored in experiments at the P and T conditions expected during subduction and serpentinization at shallow levels. It is now clear that hydrothermal diamond anvil cells are efficient tools to characterize *in-situ* aqueous systems when they are used in conjunction with spectroscopic methods such as infrared spectroscopy (e.g. Shen and

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Keppler, 1995), Raman spectroscopy (e.g. Zotov and Keppler, 2000, 2002; Mibe et al., 2008; Mysen, 2009; Mysen and Yamashita, 2010) and synchrotron X-ray fluorescence (e.g. Sanchez-Valle et al., 2003; Muñoz et al., 2005; Bureau et al., 2010).

In this work, we investigate thermal dissolution of natural siderite by experiments in hydrothermal diamond anvil cell using *in-situ* Raman spectroscopy. We have studied these reactions at low pressure (up to 1.1 GPa) and relatively low temperature conditions (i.e. ≤400 °C) since those conditions are believed to control a large part of the fluxes of H_2O and CO_2 close to the accretionary sedimentary prism of the subducting slab. These conditions are also relevant to high-temperature natural hydrothermal systems. Implications on formation of reduced carbon compounds in hydrothermal environments will be discussed.

2. Experimental methods

2.1. Hydrothermal diamond-anvil cell

Experiments were performed using an externally heated Bassett-type hydrothermal diamond-anvil cell (Bassett et al., 1993) equipped with ultra low-fluorescence type IA diamonds with 800 μm culets. Rhenium gaskets with initial thickness from 250 to 100 μm and 300-μm holes were used to contain the sample. The standard procedure for gasket preparation involved careful cleaning by multiple ultrasonic baths first in acetone and then in distilled water to prevent any contamination by organic compounds in the sample chamber. External heating was achieved using molybdenum wires wrapped around the tungsten carbide seats supporting the diamond anvils. Temperature was measured using two K-type thermocouples attached to each diamond through the heaters, allowing the temperature of each diamond to be kept constant during the experiments. Temperatures were calibrated by observing the melting points of S (112.8 °C), $NaNO_3$ (306.8 °C), CsCl (645 °C) and NaCl (801 °C). During operation, the cell was flushed with an $Ar–H_2$ (2%) mixture to prevent oxidation of diamonds and molybdenum heaters. Pressure of the sample was calculated using the equation of state (EOS) of pure water (Saul and Wagner, 1989; Duan and Zhang, 2006; Wagner and Pruss, 2002). A pressure range was calculated for $H_2O–NaCl$ following a combination of equations given by Zhang and Frantz (1987) and Brown and Lamb (1989) using the software Flincor (Brown, 1989).

In each experiment, the cell was loaded with one or two pieces (about one third to half the volume of the sample chamber, cf. Table 1) of natural siderite crystals (Siderite from Morocco, with composition ($Fe_{0.78}$ $Mg_{0.17}$ $Mn_{0.03}$) CO_3 together with de-ionized water (H_2O) or $H_2O/NaCl$ solution (NaCl 0.9 wt.%) used as an analog for seawater. Careful loading involved no air bubbles inside the sample chamber in order to reduce the initially dissolved CO_2 to negligible contents. The maximum temperature in these experiments was limited to 400 °C. Run durations were ranging from 120 to 300 min (cf. Table 1).

2.2. Raman spectroscopy

A specially designed set-up allowed to record the Raman spectra of sample chamber in the diamond-anvil cell. Raman spectra were acquired using a Jobin Yvon® HR-460 spectrometer with monochromator with 1500 gratings/mm, equipped with an Andor® CCD camera. Raman signal was excited using the 514.5 nm wavelength of an Ar^+ laser, delivering 300 mW focused into a 2 μm spot by a long-working distance Mitutoyo® ×20 objective and collected in back-scattering geometry. Backscattered Rayleigh light was filtered with a set of holographic Notch filters. Spectral resolution was about 2.5 cm^{-1}. Wave number calibration was made against neon reference lines and against the 521 cm^{-1} wavelength of silicon.

In situ measurement times were usually 60 s or 120 s per spectra in order to get reasonable signal-to-noise ratios. Some spectra were

collected in 180 s with three accumulations. Raman measurements were conducted by first recording spectra of the sample and of the fluid at ambient conditions in the diamond anvil cell. Then the sample was heated to 400 °C in about 50 °C intervals for optical and spectroscopic observations and then quenched to room temperature by rapid temperature decrease. In agreement with discussion by Zotov and Keppler (2002), Raman spectra were recorded within a few seconds after reaching the desired temperature. With this procedure, the sample chamber remained at each temperature between 20 and 30 min during Raman spectroscopy. The position of the laser spot on siderite crystal and in the fluid phase was accurately checked before and after each measurement. Background subtraction and peak fitting of Raman spectra were carried out using the Datlab software (Syassen, 2003). The Raman lines were fitted with pseudo-Voigt functions, which represent linear combination of Lorentzian and Gaussian components, in order to determine accurately the peak positions, the full width at half maximum (FWHM) and the integrated intensity. During the experiments, measurements were performed in the solutions and at the surface of the siderite crystals with a beam spot size of 2 μm.

Siderite crystals recovered after high-pressure high-temperature experiments were investigated by microRaman spectroscopy using a Renishaw inVia spectrometer. Spectra were measured at a constant room temperature (21 °C) with the 514.5 nm wavelength of a 25 mW Laser Physics Argon laser focused through a Leica microscope with a 50× objective (NA = 0.75). This configuration yields a spatial resolution of ~1 μm and a laser power delivered of ~1 mW at the sample surface. This laser power, when used in a line focus configuration, is well below the threshold that results in radiation damage to the sample. The Raman light was dispersed by a diffraction grating with 1800 grooves/mm and the signal was analyzed with a RENCAM CCD detector.

2.3. Scanning electron microscopy (SEM)

Siderite crystals recovered after high-pressure high-temperature experiments were picked up from the sample chambers and placed on carbon tape for SEM investigation. Analyses were performed with a Zeiss Ultra55 SEM, equipped with an ultra-high resolution Gemini® column. Acceleration voltage was 15 kV and beam current ranged from 10 to 20 nA. Spot resolution was 1.1 nm at 20 kV and 2.5 nm at 1 kV. Chemical analyses of the investigated areas were performed with an energy dispersion X-ray (EDX) system using a Si (Li) detector from Bruker.

3. Results

3.1. Blank experiments

In order to test the effect of possible reactions involving the rhenium gasket (Chellappa et al., 2009) and by diamond dissolution occurring at low-pressure high-temperature (see discussion by Chou and Anderson, 2009), experimental runs with pure water and saline solution were performed following the same protocol as that used with siderite crystals. Spectra were acquired every 30 °C (cf. Table 1) to carefully check the formation of carbon compounds (e.g. graphite, CO_2, CH_4,...). The results of these blank experiments at representative temperatures are reported in Fig. 1.

Water exhibits a large band in the frequency range 3000–3700 cm^{-1} assigned to the stretching vibration ν_s (e.g. Frantz et al., 1993). In the blank experiments, we observed that, with increasing temperature, the frequency at maximum intensity (ν_s) of water was shifted to higher wavenumbers and that the full width at half maximum intensity (FWHM) decreased (Fig. 1), in agreement with previous experimental studies (e.g. Chen et al., 2004).

Neither peak of methane nor of other carbon-bearing species, nor of H_2, were detected in the relevant frequency ranges upon heating at 400 °C during the 2 h of the blank runs. Therefore, reaction between the metallic (rhenium) gasket and water during experiments can be