

Experimental investigation of FeCO₃ (siderite) stability in Earth's lower mantle using XANES spectroscopy

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ABSTRACT

We studied FeCO₃ using Fe *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy at pressures up to 54 GPa and temperatures above 2000 K. First-principles calculations of Fe at the *K*-edge in FeCO₃ were performed to support the interpretation of the XANES spectra. The variation of iron absorption edge features with pressure and temperature in FeCO₃ matches well with recently reported observations on FeCO₃ at extreme conditions, and provides new insight into the stability of Fe-carbonates in Earth's mantle. Here we show that at conditions of the mid-lower mantle, ~50 GPa and ~2200 K, FeCO₃ melts and partially decomposes to high-pressure Fe₃O₄. Carbon (diamond) and oxygen are also inferred products of the reaction. We constrained the thermodynamic phase boundary between crystalline FeCO₃ and melt to be at 51(1) GPa and ~1850 K. We observe that at 54(1) GPa, temperature-induced spin crossover of Fe²⁺ takes place from low to high spin such that at 1735(100) K, all iron in FeCO₃ is in the high-spin state. A comparison between experiment and theory provides a more detailed understanding of FeCO₃ decomposition observed in X-ray absorption spectra and helps to explain spectral changes due to pressure-induced spin crossover in FeCO₃ at ambient temperature.

Keywords: Deep carbon cycle, siderite, decomposition, melting, spin transition; Earth in Five Reactions: A Deep Carbon Perspective

INTRODUCTION

Subduction zones are descending limbs of Earth's lithosphere that, together with ascending mantle plumes, are part of the active geodynamics of Earth that influence its physical and chemical evolution (e.g., Tackley et al. 1993; Zhao 2003; Walter et al. 2011; Chang et al. 2016). Subduction zones are Earth's largest recycling system. They deliver crustal material to Earth's interior, where re-equilibration with the surrounding mantle takes place mainly via complex physical mechanisms and chemical reactions (e.g., Saunders and Tarney 1984; Keppler 1996; Motti et al. 2004; Bebout 2014). Material that is not recycled in the upper few hundred kilometers of subduction zones will subduct deeper, ultimately toward the core-mantle boundary (CMB), where different temperatures, pressures, and oxygen fugacities (*f*_{O₂}) govern the stability of subducted material (e.g., Bina and Helffrich 1994; Dubrovinsky et al. 2003; McCammon 2005; Rohrbach and Schmidt 2011; Stagno et al. 2011; Bykova et al. 2016). The general structure of subducting slabs is well known and can be summarized as a layered sequence of sedimentary rocks, oceanic crust, and altered peridotite. The fate of slabs exposed to the extreme conditions present in Earth's interior is

already understood in a general way. However, a more detailed understanding requires investigation of the stability of each subducted phase to constrain the physics and chemistry of subducting plates at different depths inside Earth.

Carbonates are one of the major components of the sedimentary layers (Rea and Ruff 1996). Their presence inside Earth is supported by laboratory experiments (Stagno et al. 2011; Liu et al. 2015; Cerantola et al. 2017) and through observations of natural samples, for example inclusions in diamonds from the upper and lower mantle (e.g. Kvasnytsya and Wirth 2009; Kaminsky 2012; Kaminsky et al. 2016).

The three major carbonate components in the crust and upper mantle are CaCO₃ (calcite), MgCO₃ (magnesite), and FeCO₃ (siderite). Their presence in subducting plates (Rea and Ruff 1996) and recycled banded iron formations (Klein 2005; Konhauser et al. 2017), and their stability in experiments that simulate the paragenesis of carbonated eclogites (i.e., Kiseeva et al. 2012, 2013) suggest that they are the major source of carbon influx into the deep Earth.

Previous high-pressure studies on the carbonate end-members CaCO₃, MgCO₃, and FeCO₃ revealed high-pressure phase transitions in all three phases (i.e., Isshiki et al. 2004; Ono et al. 2005; Lavina et al. 2009; Boulard et al. 2012; Smith et al. 2018; Li et al. 2018), as well as in solid solutions between these phases (i.e., Mao et al. 2011; Merlini et al. 2012; Liu et al. 2015; Soloma-

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† Special collection papers can be found online at <http://www.minsocam.org/MSA/AmMin/special-collections.html>.

tova and Asimow 2017). In particular, iron plays a fundamental role in the behavior of carbonates at extreme conditions (e.g., Boulard et al. 2012; Liu et al. 2015). Iron can radically change the thermodynamic stability of carbonates, preserving them from breaking down at pressures and temperatures of the lower mantle. This behavior may be a direct consequence of pressure-induced electronic spin crossover (Lavina et al. 2009; Lin et al. 2012; Lobanov et al. 2015; Cerantola et al. 2015), which was reported at ~ 43 GPa and room temperature for the end-member FeCO_3 , increasing to above 50 GPa at ~ 1200 K (Liu et al. 2014).

During subduction the majority of slab geotherms intersect a deep depression along the melting curve of carbonated oceanic crust at depths of approximately 300 to 700 km (Thomson et al. 2016). FeCO_3 melting in the mantle has also been confirmed by other experimental studies (Tao et al. 2013; Kang et al. 2015) that investigated its stability from ambient conditions up to 20 GPa and ~ 2150 K. At pressures below ~ 6.8 GPa, FeCO_3 does not melt but decomposes through an auto redox dissociation reaction to Fe_3O_4 , a carbon polymorph and CO_2 (Tao et al. 2013; Kang et al. 2015). At pressures above ~ 6.8 GPa FeCO_3 melts, with a minor quenched Fe^{3+} -rich phase interpreted to be the result of redox dissociation of FeCO_3 -liquid, leading to dissolved Fe^{3+} and CO_2 in the carbonate melt (Kang et al. 2015). At $P > 33$ GPa, however, non-molecular CO_2 does not melt but dissociates to carbon and oxygen, which indicates that FeCO_3 melting at lower mantle conditions produces Fe-oxides + C (diamond) + O_2 in the melt rather than Fe-oxides + molecular CO_2 (Litasov et al. 2011). It is likely, however, that O_2 in natural settings reacts further to form other phases, i.e., bonding with available cations as a network former or modifier in the melt or forming stable crystalline phases such as oxides. Cerantola et al. (2017) recently showed that FeCO_3 melting extends up to ~ 70 GPa, where the transformation of FeCO_3 to high-pressure carbonate (HP-carbonate) structures (CO_4^{4-} groups) begins (Oganov et al. 2008; Boulard et al. 2011, 2012, 2015; Merlini et al. 2015; Cerantola et al. 2017; Merlini et al. 2017). In the same work, Cerantola et al. (2017) unambiguously showed that, after melting, FeCO_3 partially recrystallizes as $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and HP- Fe_3O_4 (Bykova et al. 2016) at pressures below and above 25 GPa, respectively. As subproducts of the reactions the presence of other Fe-oxides (minor phases) and diamond was observed (Cerantola et al. 2017). The change in the redox state of the system is likely caused by the stabilization of HP- Fe_3O_4 above 25 GPa (Dubrovinsky et al. 2003; Bykova et al. 2016). The kinetics of decomposition upon melting is still under debate and will not be discussed here.

In this study, we performed an experimental and theoretical investigation on the high-pressure high-temperature behavior of synthetic FeCO_3 using X-ray absorption near-edge structure (XANES) spectroscopy at the Fe *K*-edge. Experimental conditions covered pressures and temperatures down to the shallow-mid lower mantle and XANES data complement X-ray diffraction studies of FeCO_3 stability in Earth's mantle. In particular, XANES spectroscopy in dispersive mode is an extremely powerful experimental technique capable of detecting decomposition and phase transformation reactions on a millisecond time scale through the characteristic XANES features of the material. We acknowledge, however, the limitation of XANES in phase identification for which other complementary techniques should

be involved. In parallel, major advances in ab initio modeling techniques enable calculation of *l*-projected density of states, even in complex systems such as transition-metal oxides, to obtain theoretical simulations of the absorption spectra beyond the multiple scattering formalism (Joly 2001). The theoretical work complements our experimental findings in qualitatively reproducing the observed spectral features. Discussion of results focuses on two issues: (1) the effect of extreme conditions on FeCO_3 absorption spectra and (2) the comparison between observed and calculated XANES spectra with focus on FeCO_3 spin crossover. Finally, we extend the discussion of our experimental observations to Earth's interior and relate their importance to the fate of carbonates within the dynamics of subduction zones.

METHODOLOGY

Sample synthesis

Single crystals of $^{57}\text{FeCO}_3$ were grown from $^{57}\text{FeCO}_3$ powder at 18 GPa and 1600°C in a 1200-t Sumitomo press at Bayerisches Geoinstitut (Bayreuth, Germany). FeCO_3 powder was synthesized using ^{57}Fe -oxalate ($^{57}\text{FeC}_2\text{O}_4$) as a precursor, which in turn was obtained via chemical reactions starting from ^{57}Fe -metal (see Cerantola et al. 2015 for more details). Single crystals with an average size of $0.015 \times 0.015 \times 0.010$ mm³ were loaded together with small ruby chips 5 to 10 μm in diameter (for pressure estimation) into BX90-type diamond-anvil cells (DACs) (Kantor et al. 2012) and high-pressure membrane cells from the European Synchrotron Radiation Facility (ESRF). The Dewaele et al. (2008) pressure scale was used to estimate pressure from the fluorescence line of the ruby spheres. Diamonds with culet sizes of 250 μm and rhenium gaskets with 120 μm starting diameter holes were employed in all experiments. Neon was used as a pressure-transmitting medium and loaded at Bayerisches Geoinstitut (Kurnosov et al. 2008) and ESRF. High temperatures were achieved using the double-sided YAG laser heating system at the ID24 beamline at ESRF. Temperature uncertainties (error bars) were estimated using the difference between the measured temperature from the upstream and downstream sides of the double-sided laser heating system. To test for pressure gradients, in some experiments we placed two to three ruby chips in different positions inside the pressure chamber. In all cases, pressure differences measured by different ruby spheres loaded in the same gasket chamber were not more than 1 GPa along the entire pressure range investigated (up to 54 GPa).

XANES spectroscopy

Fe *K*-edge XANES measurements were performed at ESRF at the energy dispersive X-ray absorption spectroscopy (XAS) beamline ID24 (e.g., Pascarelli et al. 2016). The beam was focused horizontally using a curved polychromator Si 111 crystal in Bragg geometry and vertically with a bent Si mirror. The obtained cross section at the full-width half-maximum (FWHM) is about 3×5 μm^2 in horizontal and vertical directions, respectively. The Bragg diffraction peaks arising from the diamond anvils were removed from the energy range of interest by changing the orientation of the DAC and following in real time the intensity of the transmitted beam on a two-dimensional detector. The measured XANES spectra were normalized using the Athena software package (Ravel and Newville 2005), and the second-order polynomial for the pixel to energy conversion parameters was calibrated using a reference $\alpha\text{-Fe}$ foil spectrum.

Ab initio calculations

Theoretical XANES calculations were performed using the FDMNES code (Joly 2001; Bunau and Joly 2009). In FDMNES, the Schrödinger equation is solved by the finite difference method (FDM) within the local density approximation. For calculation of the spectra, structural models of FeCO_3 and HP- Fe_3O_4 were used that were based on high-pressure single-crystal X-ray diffraction (SXRD) data measured on a single crystal of FeCO_3 from the same synthesis run used to produce the samples for XANES (Table 1). SXRD measurements were carried out at the high-pressure X-ray diffraction beamline ID09a (now ID15b) at the ESRF (MAR555 detector, $\lambda = 0.4126$ Å). A FeCO_3 single crystal with an average size of $0.015 \times 0.015 \times 0.010$ mm³ was loaded and compressed to different pressures in a standard ESRF membrane cell using neon as a quasi-hydrostatic pressure medium. X-ray diffraction images were collected during continuous rotation of DACs typically from -38° to $+38^\circ$ on ω , while data collection experiments were

TABLE 1. Details of crystal structure of synthetic FeCO_3 and $\text{HP-Fe}_3\text{O}_4$ single crystal at different pressures and ambient temperature and atomic coordinates used for simulations

Sample	<i>P</i> (GPa)	<i>a</i>	<i>b</i>	<i>c</i>	Volume	α	β	γ
FeCO_3 (<i>R3c</i> , <i>Z</i> = 6)	4(1)	4.661(1)	/	15.09(5)	283.8(4)	90	90	120
	37(1)	4.530(4)	/	13.46(19)	239.2(3)	90	90	120
	55(1)	4.346(1)	/	12.4(4)	202.8(2)	90	90	120
$\text{HP-Fe}_3\text{O}_4$ (<i>Bbmm</i> , <i>Z</i> = 4)	51(1)	9.230(13)	9.168(4)	2.6775(12)	226.6(3)	90	90	90

FeCO_3 -4(1) GPa				FeCO_3 -37(1) GPa			
Site	<i>x</i>	<i>y</i>	<i>z</i>	Site	<i>x</i>	<i>y</i>	<i>z</i>
Fe	0.0000	0.0000	0.0000	Fe	0.0000	0.0000	0.0000
C	0.0000	0.0000	0.2500	C	0.0000	0.0000	0.2500
O	0.27525	0.0000	0.2500	O	0.27912	0.0000	0.2500

FeCO_3 -55(1) GPa				$\text{HP-Fe}_3\text{O}_4$ -51(1) GPa			
Site	<i>x</i>	<i>y</i>	<i>z</i>	Site	<i>x</i>	<i>y</i>	<i>z</i>
Fe	0.0000	0.0000	0.0000	Fe(1)	0.1328	0.0744	0.0000
C	0.0000	0.0000	0.2500	Fe(2)	0.3809	0.2500	0.0000
O	0.2895	0.0000	0.2500	O(1)	0.5000	0.0000	0.0000
				O(2)	0.0300	0.2500	0.0000
				O(3)	0.2210	-0.1176	0.0000

performed by narrow $0.5\text{--}1^\circ$ scanning of the same ω range. Typical images and integrated XRD patterns are illustrated in Cerantola et al. (2017) who collected comparable data on similar samples. Indexing and refinement of the unit-cell parameters were performed using CrysAlisPro software (CrysAlisPro 2014), and the complete procedure for data analysis is described in Cerantola et al. (2017).

The cluster radius for the calculations was set to 6 Å and was checked for convergence beforehand. The electron density of the potential was optimized in a self-consistent manner using the same cluster size. Calculations included quadrupolar transitions. The natural core-hole broadening of 1.4 eV was used and the value of the Fermi energy set to include excitations to d-states in the pre-edge region. Finally, calculated spectra were shifted in energy to match the experimental ones. Vibrational disorder from finite temperature was not included.

RESULTS

FeCO_3 stability as a function of pressure and temperature

The temperature effect on FeCO_3 stability at 36(1) GPa observed by XANES spectroscopy is shown in Figure 1. At room temperature before heating, a typical FeCO_3 XANES spectrum is observed with iron in the high-spin state, showing a weak pre-edge peak at 7112 eV and two main peaks, identified in the figures as “1” and “2” (Wilke et al. 2001; Cerantola et al. 2015). Heating the sample to 1890(100) K causes a decrease in the intensity of peak 2 and a smoothing of the EXAFS oscillations above 7160 eV. Upon further heating at 2270(200) K the spectrum radically changes, manifested by the loss of the double-peak structure at the main edge and the appearance of a new peak at 7113.5 eV. New features at 7155, 7173, and 7210 eV appear, drastically modifying the beginning of the EXAFS region. The flattening of the spectrum is a clear consequence of high temperature, and suggests complete or at least partial melting of the sample (e.g., Aquilani et al. 2015). The spectrum after quench shows identical features to the high-temperature spectrum, but more pronounced due to the absence of thermal damping.

Representative XANES spectra of FeCO_3 at 51(1) GPa and increasing temperature are plotted in Figure 2. In particular, Figure 2a shows low-spin FeCO_3 at room temperature with the characteristic pre-edge at 7112 eV and an additional feature at 7116.5 eV. Peak 2 is more intense than peak 1 and a pronounced hump is observed at 7155 eV (feature 3, Cerantola et al. 2015). The temperature effect is evident at 1600(100) and 1775(100) K, where an exchange of intensity between peaks 1 and 2 and a smoothing of the first EXAFS oscillation are observed. However, despite the high temperature, the characteristic pre-edge peak

position at 7112 eV is preserved. Heating to 1890(100) K and higher completely changes the spectral shape. The maximum of the pre-edge shifts from 7112 to 7113.5 eV (Fig. 3), and peak 1 shifts to slightly higher energies and “merges” with peak 2, the latter becoming a weak “hump” of the first peak. The ambient temperature spectrum after quenching from 2025(100) K (Fig. 2a, top) preserves the same features observed at high temperature, but they appear sharper due to the absence of heating.

After quenching, the same sample was re-annealed up to 1830(100) K. Annealing at lower temperature caused partial recrystallization of low-spin (LS) FeCO_3 as seen by the increase in intensity of peak 2 (Cerantola et al. 2015) up to 1675(100) K and a change in spectral shape at 1830(100) K. The XANES region of the room temperature spectrum after annealing (Fig. 2b, top) is similar to the one before heating (Fig. 2a, bottom) and is characterized by distinctive peaks marked “1”, “2”, and “3” in the spectra. The EXAFS region, however, is clearly dif-

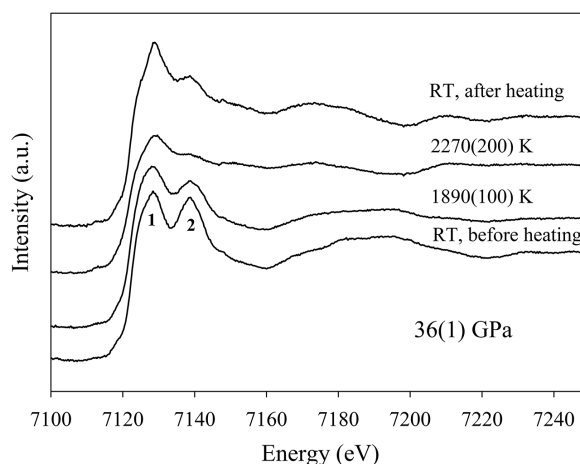


FIGURE 1. Experimental normalized XANES spectra of the Fe K-edge of FeCO_3 at 36(1) GPa and measured in situ at the indicated temperatures. Peaks marked “1” and “2” are characteristic for FeCO_3 and are used to monitor the state of the material. After heating at 2270(200) K the spectra radically change, indicating chemical and/or physical changes in the system.

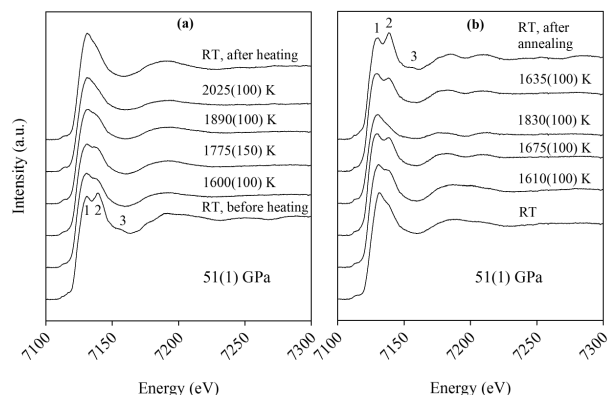


FIGURE 2. Experimental normalized FeCO_3 XANES spectra at 51(1) GPa and measured in situ at the indicated temperatures. **(a)** At room temperature, features characteristic of low-spin FeCO_3 (including the peak marked “3”; Cerantola et al. 2015) are visible. Increasing temperature stabilizes the high-spin state (marked by the intensity exchange of peaks 1 and 2 and the disappearance of peak 3), but above 1775(150) K the spectra change more drastically. **(b)** Annealing of the run product(s) at moderate temperatures shows nearly full recovery of the original spectrum after annealing but with two new humps at ~ 7185 and ~ 7210 eV.

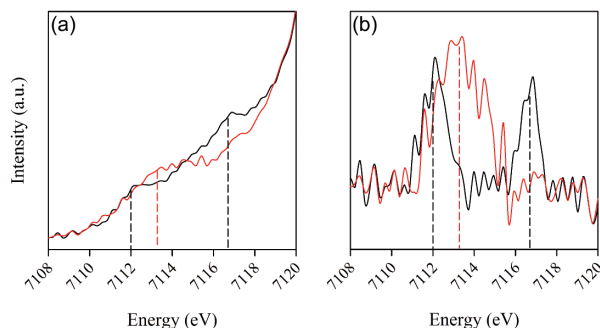


FIGURE 3. Expanded view of the pre-edge region of ambient temperature spectra at 51(1) GPa **(a)** normalized and **(b)** normalized with background subtracted. The black solid line shows the spectrum before heating in **a** and the red solid line shows the spectrum after quenching from 2025(100) K in **a**. The black curve shows a pre-edge at ~ 7112 eV and a sharp feature at ~ 7116.5 eV, which matches well with the pre-edge region in low-spin FeCO_3 (see Cerantola et al. 2015). The red curve has one broad hump at ~ 7113.5 eV that dominates the spectrum, indicating the presence of one or more Fe-containing phase(s). Note that both pre-edges in Figure 3b were normalized following the same background subtraction procedure. (Color online.)

ferent at about 7200 eV, displaying two new humps at ~ 7185 and ~ 7210 eV that are both absent in the FeCO_3 spectrum before heating (Fig. 2a, bottom).

The evolution of the XANES spectrum of low-spin FeCO_3 at 54(1) GPa and moderate temperature is shown in Figure 4. Peak 2, which is the most intense feature in the spectrum at ambient temperature, becomes progressively less intense upon heating, while peak 1 becomes the dominant peak at 1735(100) K and 1840(100) K. Moreover, high temperature causes the loss of peak 3 and the disappearance of the pre-edge peak at 7116.5 eV.

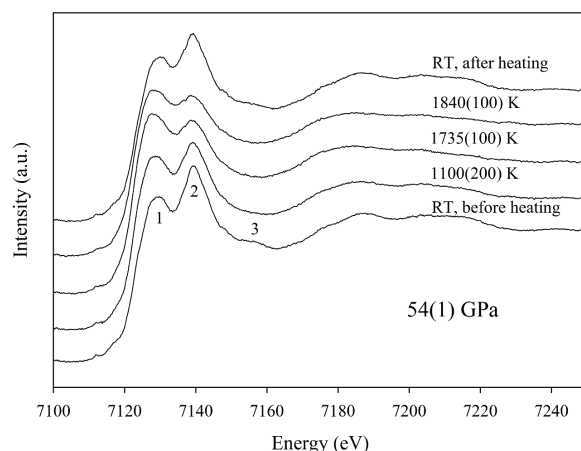


FIGURE 4. Experimental normalized FeCO_3 XANES spectra at 54(1) GPa and measured in situ at the indicated temperatures. With increasing temperature at constant pressure, iron atoms undergo a low-spin to high-spin transition, marked by a change in relative intensity of peaks 1 and 2 and disappearance of peak 3 (Cerantola et al. 2015). There is no signature indicative of decomposition reactions, and the spectrum after quenching matches closely to the spectrum before heating.

Similar to Figures 1 and 2, the high temperature tends to flatten the spectra, especially in the EXAFS region, where the characteristic features become smoother and less pronounced. Note that the room temperature spectrum after quenching matches the spectrum before heating extremely well.

XANES spectra calculated below and above spin crossover

FeCO_3 exhibits space-group symmetry $R\bar{3}c$ (calcite-group rhombohedral carbonates), where in the hexagonal setting, iron is located at the cell origin (6b), oxygen is at $x, 0, \frac{1}{4}$ (18e), and carbon is at $0, 0, \frac{1}{4}$ (6a) (Bragg 1913). The atomic arrangement can be envisioned as a distorted rocksalt structure with Fe^{2+} as the cation and CO_3^{2-} groups as the anions. The CO_3^{2-} groups form planes perpendicular to the c axis with Fe occupying the interstitial octahedral voids between the planes. No bond or polyhedral edge is parallel to the c axis.

We calculated XANES spectra of FeCO_3 by ab initio simulation using the structural lattice parameters measured by SXRD at 4, 37, and 55 GPa at ambient temperature (Fig. 5, Table 1). Qualitatively the features of the experimental spectra are reproduced well by the calculations: (1) both experimental and calculated spectra are characterized by two main peaks (identified as “1” and “2”) that shift to higher energies with increasing pressure, (2) their relative intensities also change similarly with increasing pressure, such that at 55 GPa, peak 2 is more intense than peak 1 (Fig. 5), and (3) the pre-edge feature observed at 7117 eV in the simulated spectra at 37 and 55 GPa coincides with the pre-edge feature at 7116.5 eV of the experimental spectra at similar pressures. There are some differences, however: (1) the pre-edge peak at 7112 eV in the experimental spectra (black) is not well represented in the calculated spectra (red), where instead two strong pre-edges are observed at 7115 and 7117 eV (Figs. 5a, 5b, and 5c), and (2) spectra calculated at 37 and 55 GPa are characterized by a dip at 7125 eV visible on the left side of peak 1

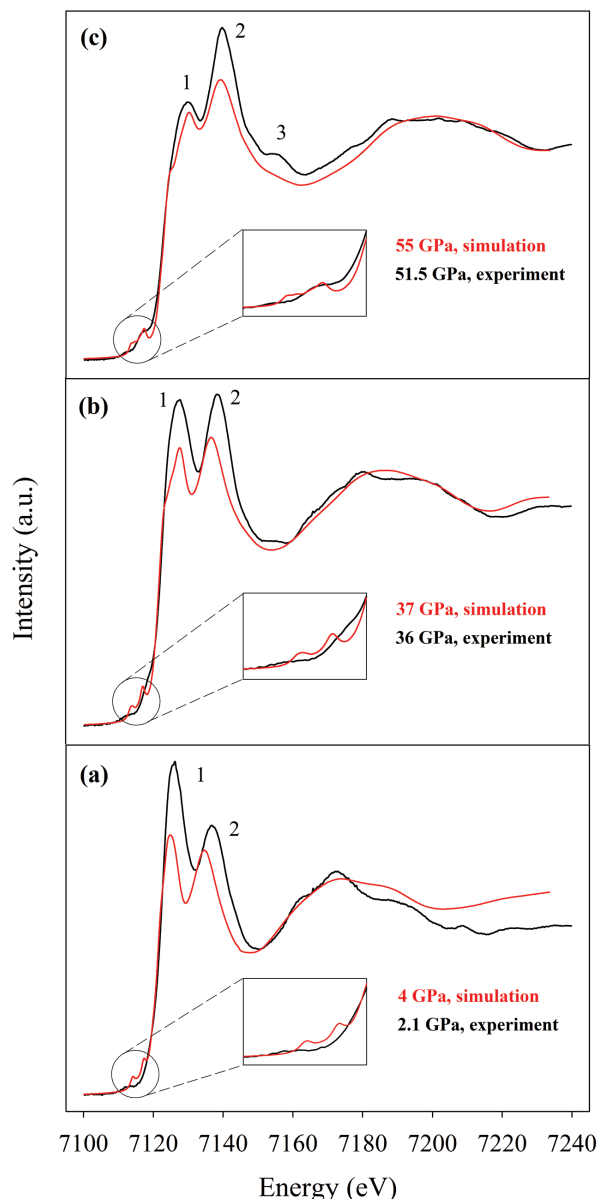


FIGURE 5. Experimental (black) and simulated (red) XANES spectra of FeCO_3 at different pressures. The insets magnify the pre-edge region. (a) Spectra show features characteristic of FeCO_3 in the high-spin state, where peak 1 is more intense than peak 2 and peak 3 is absent. Note that the pre-edge in the calculated spectrum is at 7117 eV, 5 eV higher than in the experimental spectrum, with a lower intensity feature at 7113.5 eV. (b) Spectra are characteristic for high-spin FeCO_3 just before spin crossover, where peak 2 is slightly more intense than peak 1. In the experimental spectrum a new feature appears at ~ 7116.5 eV, whereas the simulated spectrum has a pre-edge at 7117 eV and the same broad low-intensity feature at ~ 7113.5 eV. (c) After iron spin crossover, peak 2 is more intense than peak 1 and peak 3 appears in the experimental spectrum at ~ 7155 eV. Analogous to spectra at 37 GPa, the pre-edge peak in the calculated spectrum was adjusted according to the variation in the Fermi energy and in the s core level energy shift. (Color online.)

that becomes sharper with pressure, but this feature is nonexistent in the experimental spectra, which instead display a hump at 7155 eV (peak 3) that is completely absent in the simulations.

DISCUSSION

FeCO_3 melting

In a recent study, Cerantola et al. (2017) investigated the stability of FeCO_3 up to 110 GPa and $T > 2500$ K using SXRD and energy-domain synchrotron Mössbauer source (SMS) spectroscopy. At the conditions relevant for this study, $P > 36$ GPa and $T > 1850$ K, FeCO_3 melts, partially dissociating to $\text{HP-Fe}_3\text{O}_4$, diamond, and oxygen (i.e., Litasov et al. 2011). The presence of other Fe-oxide phases cannot be excluded (Cerantola et al. 2017). Electron microprobe analyses (EMPA) (Tao et al. 2013; Kang et al. 2015), SXRD, and Mössbauer spectroscopy (Cerantola et al. 2017) confirmed that even after prolonged heating the decomposition is never complete, and after quenching the presence of recrystallized FeCO_3 and $\text{HP-Fe}_3\text{O}_4$ is always observed. Note that, incomplete decomposition could be caused by pressure and temperature gradients in the DAC, however we believe this is not the case since similar behavior was observed in several studies from different authors and using various experimental techniques, such as DACs and multi-anvil apparatus (Tao et al. 2013; Kang et al. 2015; Cerantola et al. 2017).

The experimental results of the present study are consistent with Cerantola et al. (2017) (Fig. 6). At 36(1) GPa, temperatures higher than 1890(100) K (the last temperature where FeCO_3 XANES features were clearly observed, Fig. 1) cause a drastic change to the spectrum, which is interpreted to indicate complete or partial melting of FeCO_3 . Previous work has shown that melting is not stoichiometric due to partial redox dissociation of liquid FeCO_3 , leading to dissolved Fe^{3+} and CO_2 in the carbonate melt below ~ 33 GPa, whereas above ~ 33 GPa the carbonate melt recrystallizes after quenching as FeCO_3 , $\text{HP-Fe}_3\text{O}_4$, C (diamond), and O_2 (Litasov et al. 2011; Cerantola et al. 2017). A similar case is observed at 51(1) GPa and temperatures up to ~ 2000 K (Fig. 2). The intensity exchange between peaks 1 and 2 at 1600(100) and 1775(150) K is evident (Fig. 2), which is caused by the low- to the high-spin transition of Fe^{2+} (Liu et al. 2014, 2015; Cerantola et al. 2015). The characteristic pre-edge peak position at 7112 eV and the position of peaks 1 and 2 clearly indicate that at these conditions, FeCO_3 is stable and no decomposition has taken place. In contrast, the spectra at higher temperatures [collected above 1890(100) K] show a collapse of the FeCO_3 characteristic features, the most evident change is in the pre-edge that shifts from 7112 to 7113.5 eV (Fig. 3). Again, the observed changes are inferred to be caused by non-stoichiometric recrystallization due to a self-oxidation reaction during melting with the consequent formation of $\text{HP-Fe}_3\text{O}_4$ (Kang et al. 2015; Cerantola et al. 2017).

Interestingly, annealing the sample at moderate temperatures between 1610(100) and 1675(100) K caused the back reaction to occur, where partial recrystallization of LS-FeCO_3 from a mixture of $\text{HP-Fe}_3\text{O}_4$, C (diamond) + O_2 is observed (Fig. 2b). We suspect the presence of $\text{HP-Fe}_3\text{O}_4$ and possibly other Fe-oxide phases due to two humps at ~ 7185 and ~ 7210 eV in the spectra of recrystallized samples that are absent in the initial LS-FeCO_3 spectrum before heating (Fig. 2a). At 51(1) GPa, the changes in the spectra caused by heating below 1830(100) K and above

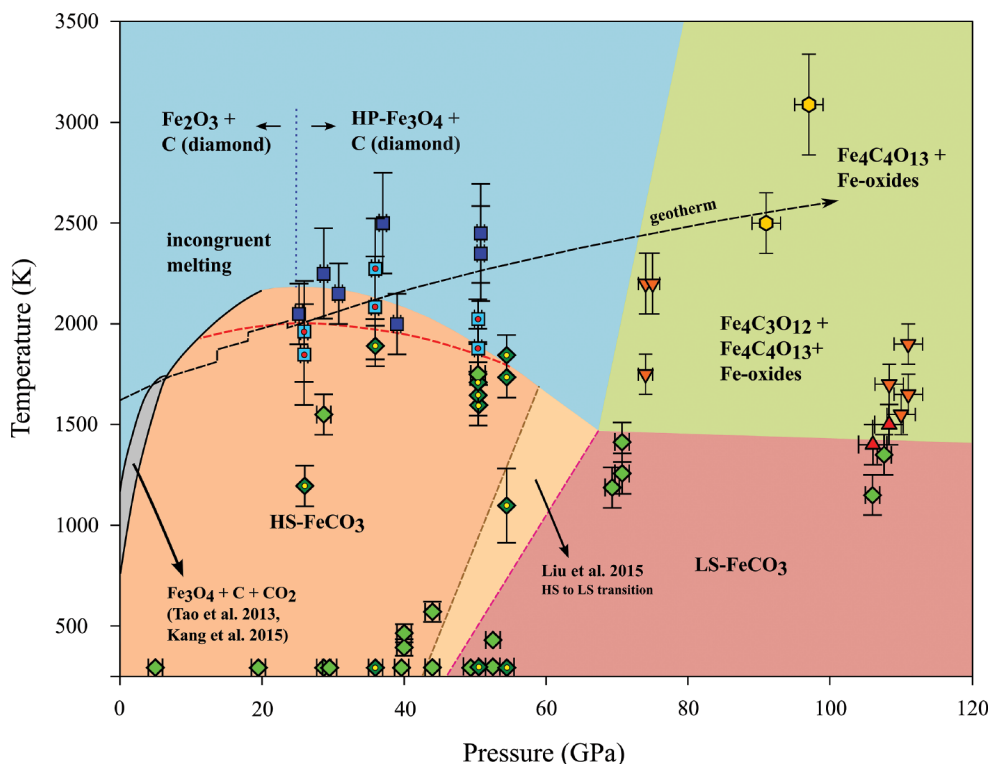


FIGURE 6. Updated stability diagram of FeCO_3 at high pressure and high temperature (modified from Cerantola et al. 2017). Symbols from this study are: dark green diamonds with yellow dot = FeCO_3 ; light blue squares with red dot = oxide(s) and recrystallized FeCO_3 . Symbols from Cerantola et al. (2017) are: light green diamonds = FeCO_3 ; blue squares = oxide(s) and recrystallized FeCO_3 ; red triangles = tetrarion (III) orthocarbonate $\text{Fe}_4\text{C}_3\text{O}_{12}$; orange inverse triangles = diiron (II) diiron (III) tetracarbonate $\text{Fe}_4\text{C}_4\text{O}_{13} + \text{Fe}_4\text{C}_3\text{O}_{12} + \text{oxide(s)}$; yellow hexagons = $\text{Fe}_4\text{C}_4\text{O}_{13} + \text{oxides}$. The shading is as follows: gray region = FeCO_3 decomposition to $\text{Fe}_3\text{O}_4 + \text{C} + \text{CO}_2$ (Tao et al. 2013; Kang et al. 2015); orange region = high-spin FeCO_3 ; red region = low-spin FeCO_3 (Liu et al. 2015); blue region = melting of FeCO_3 ; green region = formation of high-pressure carbonates $\text{Fe}_4\text{C}_3\text{O}_{12}$ and $\text{Fe}_4\text{C}_4\text{O}_{13}$ (Cerantola et al. 2017). Black dashed curve = expected mantle geotherm (Katsura et al. 2010); thick red dashed line = new boundary proposed in this study between crystalline FeCO_3 and incongruent melt; brown and violet dashed lines = spin transition region in magnesio-siderite from Liu et al. (2015) and consistent with Müller et al. (2017). A vertical dotted blue line separates the regions in which the formation of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{HP-Fe}_3\text{O}_4$ was observed upon melting of FeCO_3 . (Color online.)

1890(100) K allow us to locate the thermodynamic phase boundary between crystalline FeCO_3 and melt at about 1850 K. Results of the experiment performed at 54(1) GPa and high temperature are consistent with this conclusion (Fig. 4).

To verify our experimental observations, we simulated the XANES spectrum of $\text{HP-Fe}_3\text{O}_4$ at 51 GPa using structural data from Table 1. Figure 7a shows the calculated spectra of $\text{HP-Fe}_3\text{O}_4$ at 51 GPa (blue) and LS-FeCO_3 at 55 GPa (black). To our knowledge, there are no experimental XANES spectra of pure $\text{HP-Fe}_3\text{O}_4$ in the literature. The calculated FeCO_3 spectrum matches well with the experimental one at energies above the absorption edge (see also Fig. 5). Figure 7b shows the experimental XANES spectrum of FeCO_3 obtained after laser heating at 51(1) GPa and 2025(100) K and the sum of the calculated spectra for LS-FeCO_3 at 55 GPa and $\text{HP-Fe}_3\text{O}_4$ at 51 GPa. The similarities are evident: (1) peak 1 is more intense than peak 2, and (2) both peaks in calculated and experimental spectra are located at the same energy position. The calculated spectrum also shows a third peak (peak 3), which is clearly not present in the experimental spectrum. However, it is difficult to estimate the relative abundance for each component, which can affect

the spectral shape. We estimated a run product containing 50 wt% $\text{HP-Fe}_3\text{O}_4$ and 50 wt% LS-FeCO_3 , but the actual amount of each phase is not known. The difference in the pre-edge region can be explained by the inability of the code to simulate this feature because the pre-edge represents quadrupolar excitations to localized states.

The updated FeCO_3 stability diagram based on XANES data (Fig. 6) is largely consistent with the FeCO_3 stability fields reported by Cerantola et al. (2017). One slight difference is the position of the melting curve, which is around 200 K lower at its highest point in the updated version compared to the original diagram. While this difference is largely within the uncertainties of the temperature measurements, we note that XANES spectroscopy in dispersive mode is capable of detecting reactions on a millisecond timescale and hence the in situ measurements in the present study may provide a more accurate determination of melting compared to studies on quenched samples.

Spin crossover features from simulated spectra

Cerantola et al. (2015) first reported spin crossover in FeCO_3 observed by XANES. Here, we compare experimental data with

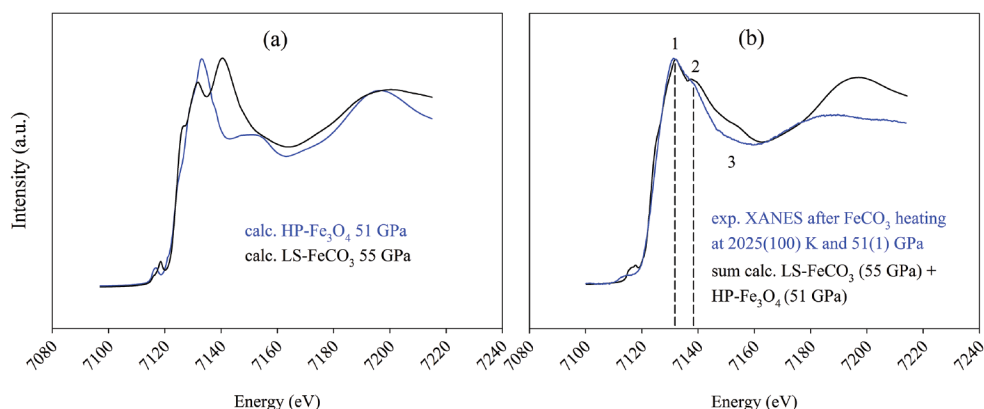


FIGURE 7. (a) Comparison between calculated XANES spectra of LS- FeCO_3 (black) and HP- Fe_3O_4 (blue). (b) Comparison between the sum of HP- Fe_3O_4 and LS- FeCO_3 calculated spectra (see Fig. 7a) (black) and the experimental spectrum after heating FeCO_3 at 2025(100) K and 51(1) GPa (blue). The presence of recrystallized HP- Fe_3O_4 after FeCO_3 (partial) melting at 51(1) was already observed using SXRD by Cerantola et al. (2017). The presence of other Fe-oxide phases cannot be excluded. (Color online.)

ab initio simulations of XANES spectra using the onset of the edge and the first EXAFS maximum. The similarity between simulated and experimental spectra is quite remarkable (Fig. 5), which can be attributed to the fact that the FDMNES code overcomes limitations from the Muffin Tin Approximation (Rehr and Albers 2000). In particular, the double peak feature at the main edge (peaks 1 and 2) has been reproduced, which is the one most indicative for the change in Fe spin state. The changes in the spectra, the broadening of the peaks, and their shift to higher energies with pressure are related to changes in the electronic structure due to shortening of Fe-O distances. The shortening is also directly seen from the shift of the first EXAFS maximum between 7170 and 7190 eV to higher energy (~20 eV), which may be described by the relation $\Delta E \times R^2 = \text{const.}$ (e.g., Bianconi et al. 1983; Wilke et al. 2007), where ΔE is the energy difference between the onset of the edge and the first EXAFS maximum and R is the Fe-O distance.

The pre-edge region at 7112 eV in the experimental spectra and at 7115 eV in the simulated spectra is related to localized $1s \rightarrow 3d$ transitions, which are quadrupolar in nature and only become dipole-allowed through hybridization of p and d orbitals for non-centro-symmetric sites. In theory, the pre-edge represents a region of the spectrum that is sensitive to changes in Fe spin as shown by Westre et al. (1997). Simulated spectra do show slight differences in this energy region between high-spin and low-spin state; however, a comparison with experimental spectra is difficult due to low resolution and low statistical quality of the data in this region. The feature at 7116.5 eV, which emerges in the experimental spectra at and above spin crossover, is likely related to excitations of $1s$ to $4p$ electron states of the valence band (e.g., Caliebe et al. 1998). This feature becomes better resolved at higher pressures because the main edge shifts to higher energy due to decreasing Fe-O distance. In the simulations, this feature is also at ~7117 eV and becomes better resolved due to the shift of the main edge to higher energy, similar to experiment. Likewise, the depression at around 7125 eV present in the simulated spectrum at 37 and 55 GPa is also related to the shortening of the Fe-O distance upon compression and spin crossover, so that the feature is more pronounced and sharper at 55 GPa than at

37 GPa due to the shift of the main edge. At higher energy, the presence of the hump at ~7155 eV (feature 3) in the experimental spectra above 37 GPa is not observed in the simulations, which suggests that this feature stems from multiple scattering and cannot be adequately reproduced by the calculation performed here (Fig. 5). Overall, the theoretical spectra and analysis of the l -projected density of states show that the changes in the main-edge XANES region of the spectra are mainly related to the shift of p -states to higher energies, which is induced by the reduction of the Fe-O distance.

Methods for ab initio simulation of XANES spectra still have shortcomings when compared to experiments (Rehr and Albers 2000; Joly 2001; Bunau and Joly 2009). Interactions of the photoelectron with electronic states of the host close to the edge are quite complex and thus the fine structure cannot always be fully replicated. In particular, excitations to localized states are known to be less well-described by real-space calculations, particularly if they are quadrupolar in nature. Furthermore, the core-hole screening is only approximated. This may substantially shift or suppress features in the calculated spectrum. Finally, these calculations did not include effects caused by thermal disorder to avoid broadening of observed features that were the main focus of our study.

IMPLICATIONS

Carbonate-bearing subducting slabs have different thermal profiles, which mainly vary based on slab age and velocity of subduction. Colder slabs subduct faster mainly due to their enhanced density (e.g., Syracuse et al. 2010). Recently, it has been proposed that the majority of slab geotherms intersect a deep depression along the melting curve of carbonated oceanic crust at depths of approximately 300 to 700 km during subduction (Thomson et al. 2016). At those depths, FeCO_3 melts, forming $\alpha\text{-Fe}_2\text{O}_3$ below ~25 GPa (Kang et al. 2015; Cerantola et al. 2017) and HP- Fe_3O_4 at higher pressure (depths below 750 km) (Cerantola et al. 2017). These redox dissociations are accompanied by the formation of other compounds such as diamond, oxygen, and possibly Fe-oxides with different stoichiometry. FeCO_3 incongruent melting has important implications for the influx of carbon via Fe-car-

bonates inside Earth, because it provides a mechanism for FeCO_3 to partly survive even in subducting plates with higher thermal regimes, which promotes subduction to the deepest regions of Earth's mantle. For instance, FeCO_3 -rich carbonated liquids that escape from subducting plates can recrystallize to solid FeCO_3 in the proximity of colder regions in the lower mantle, stagnating there and being subject of deep Earth's geodynamic phenomena, such as further downwelling or upwelling.

In this study, we investigated the melting of FeCO_3 at high pressure and high temperature. Based on our results, we suggest that subducting slabs with average surface temperature (~ 1250 K at 15 GPa; Syracuse et al. 2010) will undergo carbonate-melting processes (Thomson et al. 2016) that result in partial FeCO_3 decomposition to oxides and diamond. In contrast, subducting slabs with lower surface temperature (~ 1050 K at 15 GPa; Syracuse et al. 2010 or 1500 K at 70 GPa; e.g., Kaneshima and Helffrich 2003; Komabayashi et al. 2009) could survive subduction through Earth's mantle without undergoing melting until pressures and temperatures were high enough to cause transformation of CO_3^{2-} -carbonates to their high-pressure structures characterized by CO_4^{4-} tetrahedra above 70 GPa (Merlini et al. 2015, 2017; Cerantola et al. 2017).

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