American Mineralogist, Volume 104, pages 1083–1091, 2019

Experimental investigation of $FeCO_3$ (siderite) stability in Earth's lower mantle using XANES spectroscopy

Valerio Cerantola[1,2,*,†], Max Wilke[3], Innokenty Kantor[4], Leyla Ismailova[5], Ilya Kupenko[6], Catherine McCammon[2], Sakura Pascarelli[1], and Leonid S. Dubrovinsky[2]

[1]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
[2]Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany
[3]Institut für Erd- und Umweltwissenschaften, Universität Potsdam, Karl-Liebknecht-Straße 24, 14476 Potsdam, Germany
[4]Danmarks Tekniske Universitet, Anker Engelunds Vej 1 Bygning 101A, 2800 Kgs. Lyngby, Denmark
[5]Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Building 3, Moscow, 143026, Russia
[6]Institut f. Geowissenschaften, Universität Münster, Schlossplatz 2, 48149 Münster, Germany

Abstract

We studied $FeCO_3$ 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 $FeCO_3$ were performed to support the interpretation of the XANES spectra. The variation of iron absorption edge features with pressure and temperature in $FeCO_3$ matches well with recently reported observations on $FeCO_3$ 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, $FeCO_3$ melts and partially decomposes to high-pressure Fe_3O_4. Carbon (diamond) and oxygen are also inferred products of the reaction. We constrained the thermodynamic phase boundary between crystalline $FeCO_3$ and melt to be at 51(1) GPa and ~1850 K. We observe that at 54(1) GPa, temperature-induced spin crossover of Fe^{2+} takes place from low to high spin such that at 1735(100) K, all iron in $FeCO_3$ is in the high-spin state. A comparison between experiment and theory provides a more detailed understanding of $FeCO_3$ decomposition observed in X-ray absorption spectra and helps to explain spectral changes due to pressure-induced spin crossover in $FeCO_3$ at ambient temperature.

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