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High-pressure polymorphs of ferroan dolomite: Possible host structures for carbon in the lower mantle

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Abstract

In this study, we investigated four different ferroan dolomite samples using in situ Raman spectroscopy and powder X-ray diffraction (XRD) at pressures up to 48 GPa and room temperature. Our results show that the transition from Dolomite-I (Dol-I) to Dolomite-II (Dol-II) occurs above 13–16 GPa, and the transition pressure depends on the composition of the solid solution. Compression above 32–35 GPa results in the appearance of Dolomite-IIIc (Dol-IIIc) or Dolomite-IIIb (Dol-IIIb). In the high-pressure XRD study, we found that the XRD patterns of $Ca_{0.97}(Mg_{0.77}Fe_{0.23}Mn_{0.03})(CO_3)_2$ (xFe = 0.23, Ank23) can be indexed as Dol-IIIc at 44 GPa, while the rhombohedral Dol-IIIb structure matches better with the XRD patterns of the xFe = 0.40 (Ank40) and 0.64 (Ank64) solid solutions. Additionally, in the Raman spectra of the Fe-richest sample (Ank64), we observed an abrupt frequency downshift of the CO_3-stretching vibrations between 40–42 GPa, which may reflect a pressure-induced Fe^{2+} spin transition.

We further investigated two samples with xFe = 0.19 (Ank19) and 0.23 (Ank23) at high pressure and high temperatures, up to at least 2600 K. The experiments revealed that the unquenchable Dol-IIIc structure could be a stable high-pressure/high-temperature polymorph in ferroan dolomite up to at least 2600 K.

Keywords: Deep carbon cycle, dolomite, solid solution, phase diagram, phase transition, high pressure, Raman spectroscopy