



	Experiment title: Cation disorder in dolomite, $\text{CaMg}(\text{CO}_3)_2$, and its influence on the aragonite + magnesite \leftrightarrow dolomite reaction boundary	Experiment number: HS2130
Beamline: ID30	Date of experiment: from: 12 May 2003 to: 18 May 2003	Date of report: Feb. 13 2004
Shifts: 12	Local contact(s): Dr. W. A. Crichton	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): SYTLE M. ANTAO ^{1*} , JOHN B. PARISE ^{1*} , WILSON A. CRICHTON ^{2*} , WILLEM, H. MULDER ³ , AND ISHMAEL HASSAN ^{3*} ¹ Mineral Physics Institute & Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100, USA ² European Synchrotron Radiation Facility, BP 220, F 38043 Grenoble, France ³ Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica		

Introduction

Phase relations in the geologically important $(\text{Ca,Fe,Mg})\text{CO}_3$ system are dominated by interactions among the disordered calcite-structure solutions and the ordered dolomite structure where Ca and (Mg, Fe) cations order into sites in alternating layers. Recent results suggest that dolomite maybe stabilized to high pressures [1] through phase transitions and at high pressures (P) and temperatures (T) due to cation disorder [2-4]. These results impact on the reservoir for carbonate in the mantle, issues of carbon cycling in the planet and the $f(\text{CO}_2)$ in the earth's interiors since dolomite may be the stable carbonate throughout the mantle. Our experiments at high pressures and temperatures determined the structure of dolomite at 3 GPa and from 298 to 1466 K [5]. We were able to construct a consistent thermodynamic model for the cation disordering process. The study (described in more detail below) also suggested full Rietveld structure refinement rather than the intensity of "ordering" reflections" more reliably characterizes the degree of cation disorder at any particular condition of P and T . Of course the study also confirms the obvious, that the disappearance of ordering reflections is an accurate marker for complete disorder as it must, as this transition involves a transition from space group ($R\bar{3}$) to that of calcite ($R\bar{3}c$). These very preliminary and encouraging results however raise a number of intriguing questions, amongst them is the affect of higher pressures (does pressure favour disordering as earlier quench experiments in the $(\text{Ca,Fe})_2\text{CO}_3$ system suggest [6]?); and what are the effects of Fe? Additionally, the prospect of increased scattering contrast in the dolomite-related system $\text{CdMg}(\text{CO}_3)_2$ suggests a more accurate determination of the progress of

disorder as a function of P and T , and the thermodynamic model to describe it, will provide further insight into the dramatic rise in stability of the carbonates at high P and T .

Experimental details

In situ high- P and high- T data were collected in a Paris-Edinburgh large-volume apparatus [7] ($\lambda = 0.3738(4)$ Å). The cross-calibration techniques [7] determined the P and T conditions at which each imaging plate (IP) pattern was collected on Mar Research Mar345 IP detector. Data, integrated with Fit2D [8], were obtained using a multi-channel collimator to eliminate parasitic scattering from the high- P cell assembly [9].

Results

Data analyzed with the Rietveld method provided values of the order parameter s , defined as $s = 2x_{\text{Ca}}^a - 1$ where x_{Ca}^a is the mole fraction of Ca^{2+} ions on the sub-lattice. The value of s varies between 1 (complete order) at room P and T and 0 (complete disorder) at the highest temperatures (see Fig. 1). From a thermodynamic point of view, this system shows a strong resemblance to binary alloys, which suggests a description in terms of the mean-field Bragg-Williams (BW) model (Fig. 1).

The s obtained by Rietveld structure refinement is more reliable than the intensity method where the ratio of intensities of reflections (015) and (006) is used as a measure of s .

Having determined s in dolomite as a function of P and T and having more accurately determined the T at which complete disorder occurs, several new areas of investigation unfold. These include the P -dependence of ordering. Attempts to fit the breakdown curve for aragonite + magnesite \leftrightarrow dolomite ($\text{CaCO}_3 + \text{MgCO}_3 \leftrightarrow \text{CaMg}(\text{CO}_3)_2$) based upon the data we have obtained suggests that either T_c (the T of disorder) or the constant a (Fig. 1) must change as a function of P . More intriguing is

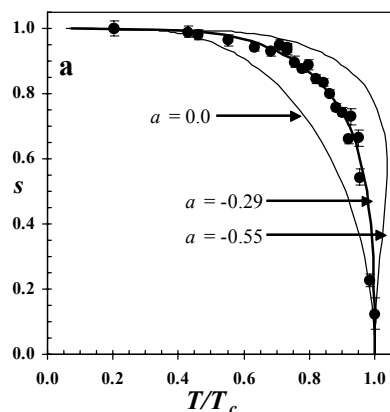


Fig. 1. Results for the order parameters, s , determined from Rietveld refinements of data collected on dolomite at high P and T . Fits of a modified Bragg-Williams treatment to derive a thermodynamic model for the order-disorder transition are overlaid for values of the modifier $a = 0.0, -0.29$, and -0.55 .

the report from colleagues in our laboratories [6] that *disorder* is favoured at higher pressures in the $(\text{Ca},\text{Fe})\text{CO}_3$ system. Finally, recent reports of a phase transition in dolomite at around 20 GPa (far above our present study at 3 GPa) suggests disorder in that phase needs careful examination. Our initial experiments show that Rietveld refinements using carefully collected monochromatic data on ID30 provide a firm experimental basis to explore some of these intriguing problems and straight forward thermodynamic modelling can be applied to the results.

References

1. Santillan, J., Q. Williams, and E. Knittle, *Geophys. Res. Lett.*, 2003. **30**(2): p. 1054-1057.
2. Luth, R.W., *Contrib. Min. Pet.* 2001. DOI 10.1007/s004100100238: p. (online version).
3. Luth, R.W., EOS, Trans. AGU, 1999. **Suppl. 80**: p. 350.
5. Antao, S.M., Hassan, I., Crichton, W., & Parise, J.B., *Am. Mineral.*, 2004. **Submitted**.
6. Davidson, P.M., et al., *Geochem. Cosmochem. Acta*, 1993. **57**(23-24): p. 5105-5109.
7. Crichton, W.A. and M. Mezouar, *High Temp. High Press.*, 2002. **34**(2): p. 235-242.
8. Hammersley, A.P., et al., *High Press. Res.*, 1996. **14**: p. 235-248.
9. Mezouar, M., et al., *Rev. Sci. Instrum.*, 2002. **73**(10): p. 3570-3574.