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Properties of molten $CaCO_3$ at high pressure

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Supplementary Information

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- Material and Methods
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Material and Methods

Pure $CaCO_3$ powder (>99.0 %, Sigma Aldrich) was pre-packed as a cylinder and loaded in a graphite capsule. A detailed description of the Paris-Edinburgh press experimental techniques and cell design can be found in Kono *et al.* (2014). Recovered quenched sample was analysed by scanning electron microscopy to check the physical and chemical integrity of the sample throughout the experiments (Fig. S-1).

Pressure was determined from the cell-volume change of the pressure transmitting medium in the form of an MgO cylinder. Temperature was estimated by previous power calibrations using this cell assembly (Kono *et al.*, 2014). This calibration also accounts for the effect on pressure of the distance between the sample and MgO ring at high temperature using the *P-V-T* relation of MgO and elastic wave velocity measurements (Kono *et al.*, 2010). Diffraction patterns on the MgO were collected before and after data collection on the sample, to monitor any variation of T that might have occurred. X-ray diffraction was collected for 2 hours using an energy-dispersive germanium solid-state detector at ten 2 angles (2°, 2.7°, 3.5°, 5°, 7°, 10°, 15°, 20°, 27°, 35°) enabling coverage up to 20 $Å^{-1}$ in reciprocal space with $Q = 4\pi E \sin\theta/12.398$, where E is the energy of the X-rays in keV up to >100 keV. Bragg peaks arising from the diffraction of graphite in the cell assembly, and fluorescence of indium on the detector were removed at each angle. The structure factor, S(q), was derived from the X-ray diffraction patterns using the aEDXD program developed by Changyong Park (Kono *et al.*, 2014).

Density of $CaCO_3$ melts is calculated assuming a C-O coordination number of 3, from the area below the C-O contribution on radial distribution functions as $g(r)$ is a function of the density (Eq.1) using the following equations

$$g_{C-O}(r) = \frac{A_{C-O}}{nS_\infty \sigma_i \sqrt{2\pi}} exp\left(-\frac{(r-d_{C-O})^2}{2\sigma^2}\right) \quad \text{Eq. S-1}$$

$$A_{C-O} = \frac{CN_{C-O}}{\int \frac{4\pi r^2}{\sigma\sqrt{2\pi}} exp\left(\frac{-(r-d_{C-O})^2}{2\sigma^2}\right) dr} \quad \text{Eq. S-2}$$

where $CN_{C\text{-}O}$ is the coordination number of the C-O contribution, *i.e.* 3, d_{C-O} the inter-atomic distance, and $\sigma = k\sqrt{d_{C-O}}$ a parameter depending on structural disorder (Hosemann and Bagchi, 1962) where k is an adjustable parameter set to 0.08.

$$S(q) = n\sum_{i,j} c_i c_j f_{i,j}(q) \int_0^{\infty} r(g_{i,j}(r) - 1) \frac{\sin(qr)}{k} dr \quad \text{Eq. S-3}$$

with

$$f_{i,j}(q) = \frac{f_i(q) f_j(q)}{[\sum_i \text{cifi}]^2} \quad \text{Eq. S-4}$$

where c_i is the mole fraction of species i, and f_i is the atomic scattering factor tabulated from Hajdu (1972). To extrapolate *S(q)* to q = 0 Å^{-1} (Fig. S-2), we use

$$S(q) = a_0 \exp(a_1 q) + a_2 \quad \text{Eq. S-5}$$

with a cut-off intensity of 0.275, where a_0, a_1 and a_2 are fitting parameters.

Supplementary Tables

Table S-1 Summary of high pressure runs. *P* indicated are the mean values between *P* measured before and after data collection on the melt.

P (GPa)	*T* (K)	n_0 (Å^{-3})	Density (kg/m^{-3})
2.4 (2)	1773	0.0690(5)	2294(50)
3.5 (2)	1923	0.0710(5)	2361(50)
4.7 (3)	2073	0.0720(5)	2401(50)
7.4 (4)	2073	0.0750(5)	2494(50)
8.7 (1)	2073	0.0785(5)	2610(50)

Supplementary Figures

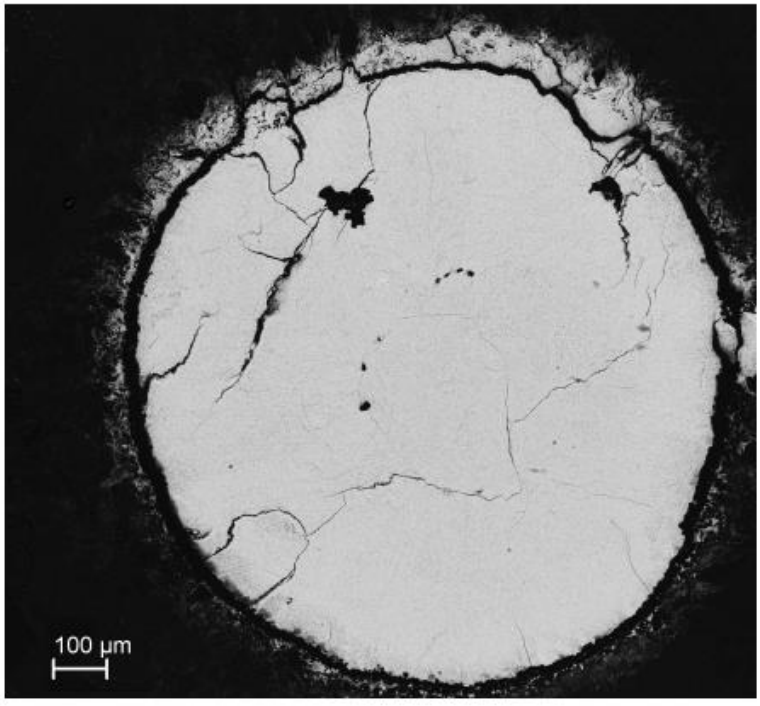

Figure S-1 SEM image of recovered $CaCO_3$ sample, the cross section is perpendicular to the sample cylindrical axis.

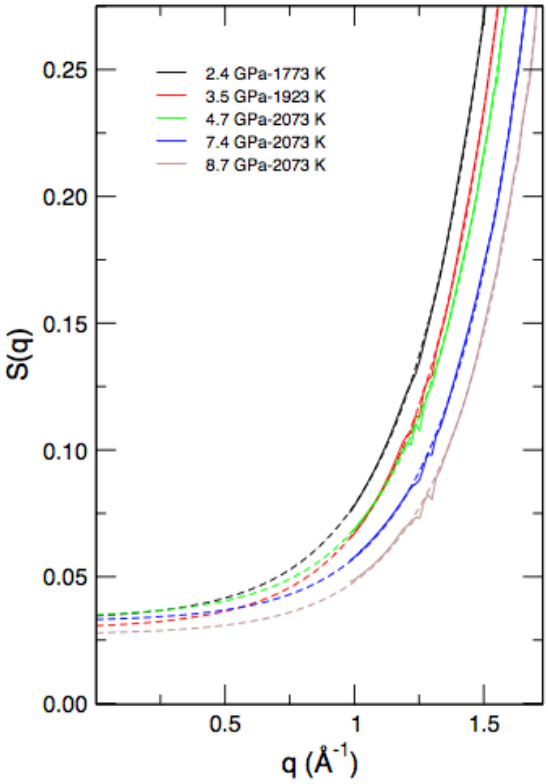

Figure S-2 Extrapolation of *S(q)* towards *q*=0 Å^{-1}; plain curves: experimental *S(q)*, dashed lines: fit to the data using Eq. S-5.

Supplementary Information References

Hajdu, F. (1972) Revised parameters of the analytic fits for coherent and incoherent scattered x-ray intensities of the first 36 atoms. *Acta Crystallographica* A28, 250-252.

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Kono, Y., Irifune, T., Higo, Y., Inoue, T., Barnhoorn, A. (2010) P-V-T relation of MgO derived by simultaneous elastic wave velocity and in situ x-ray measurements: A new pressure scale for the mantle transition region. *Physics of the Earth and Planetary Interiors* 183, 196–211.

Kono, Y., Park, C., Kenney-Benson, C., Shen, G., Wang, Y. (2014) Toward comprehensive studies of liquids at high pressures and high temperatures: Combined structure, elastic wave velocity, and viscosity measurements in the Paris-Edinburgh cell. *Physics of the Earth and Planetary Interiors* 228, 269–280.