Supplemental Materials

Implications of high-pressure oxygen hydrates on radiolytic oxygen in Jovian icy moons

Mungo Frost,[1] Mikhail Kuzovnikov,[2] Philip Dalladay-Simpson,[3,4] Ross T. Howie,[2] John S. Loveday,[2] Umbertoluca Ranieri,[2] and Eugene Gregoryanz[2,4,5]

[1]*High Energy Density Sciences Division, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, USA*[*]

[2]*Centre for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, King's Buildings, EH9 3FD, Edinburgh, UK*

[3]*Center for High Pressure Science and Technology Advanced Research, 1690 Cailun Road, Shanghai, 201203, China*

[4]*SHARPS (Shanghai Advanced Research in Physical Sciences), 68 Huatuo Rd, Pudong, Shanghai, 201203, China*

[5]*Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China*

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[*] mdfrost@slac.stanford.edu

SUPPLEMENTARY NOTE I. STRUCTURAL DATA

Tables give details of fitted atomic positions for each phase based on Rietveld refinement.

A. CS-II

Space group $Fd\bar{3}m$ (n. 227, origin at $\bar{4}3m$), $a = 17.183(4)$ Å at 0.22 GPa.

Atom	Site	x	y	z	U_{iso}, Å^2	Occ.
O	8a	0	0	0	0.10(3)	1
O	32e	0.908(3)	0.908(3)	0.908(3)	0.10(3)	1
O	96g	0.942(2)	0.942(2)	0.756(3)	0.10(3)	1
Guest 1 O	16c	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.30(13)	1.7(3)
Guest 2 O	96g	0.564(8)	0.564(8)	0.499(15)	0.3(4)	0.26(7)

B. ST

Space group $P4_2/mnm$ (n. 136), $a = 6.298(1)$ Å, $c = 10.703(2)$ Å at 1.4 GPa.

Atom	Site	x	y	z	U_{iso}, Å^2	Occ.
O	4d	0	$\frac{1}{2}$	$\frac{1}{4}$	0.08(2)	1
O	8j	0.654(4)	0.654(4)	0.128(3)	0.08(2)	1
Guest O	8i	0.14(1)	0.78(1)	0	0.13(fixed)	0.76(5)

C. C_0

Space group $P3_112$ (n. 151), $a = 6.218(2)$ Å, $c = 6.273(4)$ Å at 1.8 GPa.

Atom	Site	x	y	z	U_{iso}, Å^2	Occ.
O	3a	0.24(1)	0.76(1)	$\frac{1}{3}$	0.03(3)	1
O	3b	0.76(1)	0.24(1)	$\frac{5}{6}$	0.03(3)	1
Guest O	6c	0.95(4)	0.13(3)	0.30(3)	0.03(7)	0.55(10)

D. MH-III Like

Space group *Imma* (n. 74), $a = 8.034(2)$ Å, $b = 4.678(1)$ Å, $c = 7.706(2)$ Å at 2.3 GPa.

Atom	Site	x	y	z	U_{iso}, Å^2	Occ.
O	8i	0.171(3)	$\frac{1}{4}$	0.406(4)	0.05(1)	1
Guest O	8i	0.454(9)	$\frac{1}{4}$	0.667(5)	0.15(4)	0.83(6)

VOLUME PER WATER MOLECULE, c/a AND b/a RATIOS

Figure S1 shows the volume per water molecule and ratio of the crystal axes fitted from powder x-ray diffraction for the oxygen hydrate phases with pressure. The volume per water molecule increases for higher pressure phases, particularly the MH-III like phase, due to increasing guest O_2 concentration. c/a ratios are shown for the tetragonal ST clathrate and hexagonal C_0 hydrate phases, and c/a and b/a are shown for the orthorhombic MH-III like filled ice.

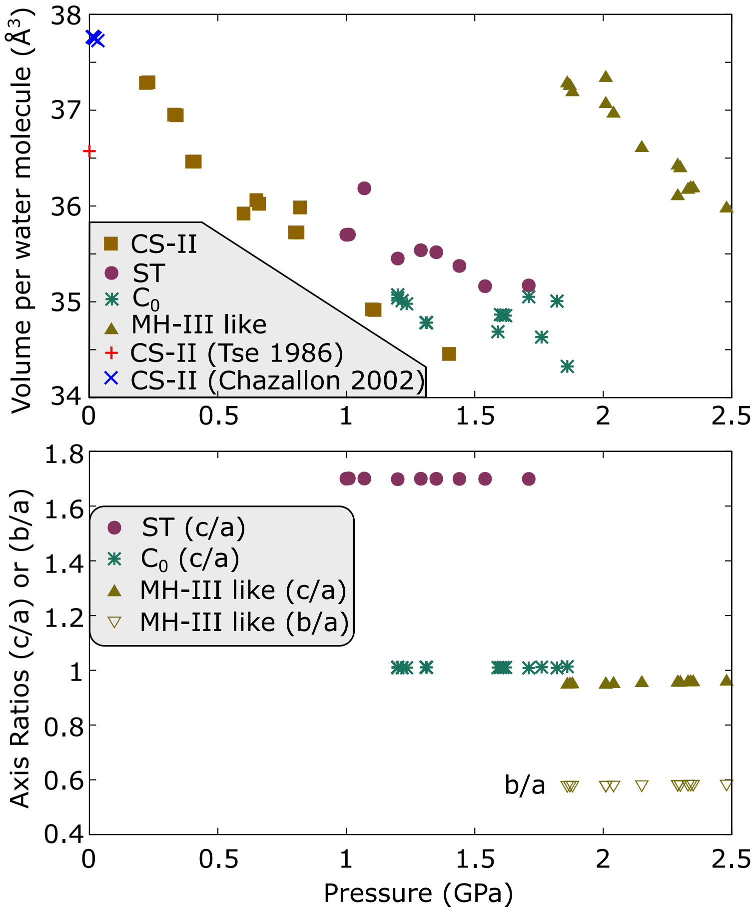

FIG. S1. **Top:** volume per water molecule for the various phases plotted against pressure. Literature data for the CS-II phase at low pressure from Tse *et al.* [18] and Chazallon *et al.* [19] are also shown. **Bottom:** Ratios of the crystallographic axes for the various phases plotted against pressure.

O-H STRETCH MODE

Figure S2 shows the pressure evolution of the O-H stretch Raman feature on compression at 66 K. Above 1.87 GPa, the low-frequency peak is lost and the feature becomes very broad, which is compatible with pressure-induced collapse and amorphization of the clathrate.

Figure S3 shows full Raman spectra of each oxygen hydrate phase at 298 K including the O-H stretch in the region of 2500 to 3000 cm^{-1}.

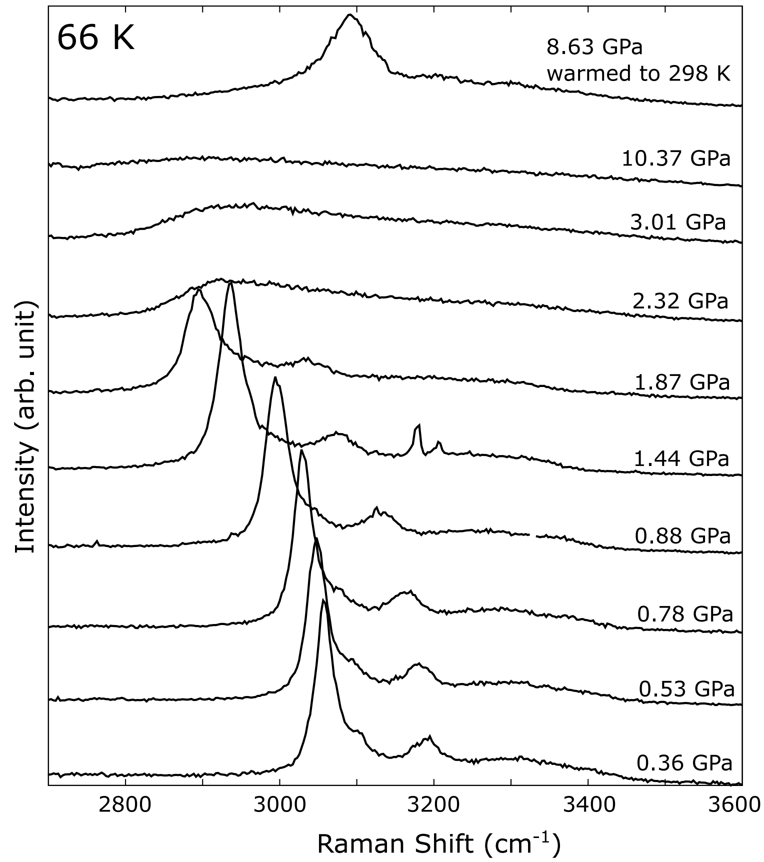

FIG. S2. Pressure evolution of the O-H Raman feature at 66 K. Top trace shows sample after warming to ambient temperature.

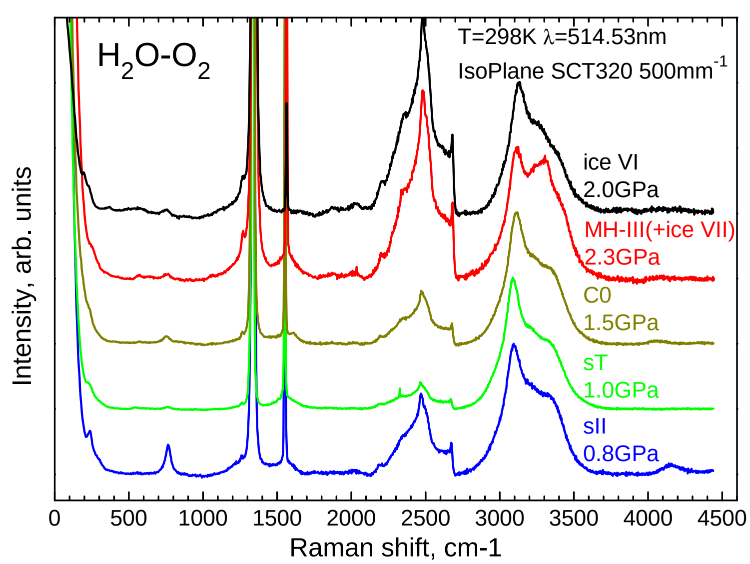

FIG. S3. Full Raman spectra of oxygen hydrate phases at 298 K.

SUPPLEMENTARY NOTE II. DETAILS OF EUROPAN OXYGEN CAPACITY CALCULATION

The radius of Europa is 1561 km, and it has an outer ice shell thickness of 30 km [46, 55]. Estimates of this thickness vary moderately and this is the dominant source of uncertainty. The volume of this shell is $\sim 9 \times 10^8$ km^3. Ignoring the effect of compression within the first 30 km ice has density 997 kg/m^3, giving this layer a mass of $\sim 9 \times 10^{20}$ kg. This is expressed in Equations 1 and 2:

$$V_{ice} = \frac{4\pi}{3}\left(r_{Europa}^3 - (r_{Europa} - t_{ice})^3\right) \tag{1}$$

$$m_{ice} = V_{ice}\rho_{ice} \tag{2}$$

At low pressure, CS-II oxygen hydrate hosts around 0.16 oxygen molecules per water molecule (Figure 5 in main text), which accounting their molecular masses equates to water being able to host about 28% of its mass in oxygen as a CS-II clathrate, as can be obtained from Equation 3:

$$\frac{m_{O_2}}{m_{H_2O}} = n\frac{M_{O_2}}{M_{H_2O}} \tag{3}$$

where n is the number of guest O_2 molecules per water molecule, m_x is the mass of component x, and M_x is the molar mass of compound x. This gives a maximum oxygen capacity for a 30 km ice shell on Europa of 2.5×10^{20} kg.

Multiplying the measured rate of radiolytic O_2 production, 12 kg/s [8], by the age of the solar system, 4.57 Gyr ($= 1.44 \times 10^{17}$s), gives a total oxygen production, assuming the rate has not varied substantially over time, of around 1.7×10^{18} kg, which is <1% of the total estimated maximum oxygen absorption capacity.

Numbered references match those in main text.