How does a crystal melt? How long does it take for melt nuclei to grow? The melting mechanisms have been addressed by several theoretical and experimental works, covering a subnanosecond time window with sample sizes of tens of nanometers and thus suitable to determine the onset of the process but unable to unveil the following dynamics. On the other hand, macroscopic observations of phase transitions, with millisecond or longer time resolutions, account for processes occurring at surfaces and thus limited by thermal contact with the environment. Here, we fill the gap between these two extremes, investigating the melting of ice in the entire mesoscopic regime. A bulk ice I$_h$ or ice VI sample is homogeneously heated by a picosecond infrared pulse, which delivers all of the energy necessary for complete melting. The evolution of melt/ice interfaces thereafter is monitored by Mie scattering with nanosecond resolution, for all of the time needed for the sample to reequilibrate. The growth of the liquid domains, over distances of micrometers, takes hundreds of nanoseconds, a time orders of magnitude larger than expected from simple H-bond dynamics.

Mie scattering | temperature jump | superheating | laser heating | anvil cell

Melting of ice is one of the most common occurrences on our planet, from polar ices to glaciers, to the morning frost and the preparation of our drinks. Ices are present as well in extraterrestrial environments, planetary and intersellar, going through extremely different pressure and temperature conditions, where many phase boundaries are encountered. The molecular mechanisms of melting and the characteristic timescales of the process are not well elucidated, as for any other phase transition. In fact, great effort is presently being made with state of the art experimental techniques to understand the intrinsic kinetics of structural transformations, particularly under dynamic compression, by which phase-transition boundaries up to extreme pressures ($P$) and temperatures ($T$) can be accessed (1–6). Melting is the least hindered of phase transitions, requiring the disruption of the crystalline order and the achievement of the local structure of the liquid phase.

The dynamics of melting have been studied up to the present in the picosecond timescale, observing structural changes on a length scale of few nanometers, in the attempt to explain the fundamental mechanisms of the transition onset. In both simulations and experiments, micrometric- or submicrometric-sized crystals can be rapidly heated above the melting temperature ($T_{m}$), into a superheated state where melting occurs. Metals and water ice have been the test systems. Simulations have revealed a nucleation and growth mechanism (7–11), and nucleation has been especially addressed, in trying to determine the minimum number of atoms/molecules needed to form a critical nucleus for the transitions, the solid/melt interfacial energy, the transient local structures achieved during the transformation, and the role of defects and surfaces. Experimentally, the sample can be rapidly heated by a pulse of infrared light at a wavelength that the sample can absorb ($T$ jump). With this "direct laser heating" the sample is heated from within, and transition nuclei can be formed in the bulk, overcoming the dominance of heterogeneous nucleation, induced by surfaces or preexisting defects (12).

The temperature increases by the redistribution of the absorbed energy via the vibrational relaxation over the lattice modes. This thermalization process takes $\sim$20 ps in water ice (13) and can be slower in non–H-bonded molecular crystals. The structural changes following the heating pulse have been monitored in aluminum (14) and gold (15) by electron diffraction with a sample thickness of 20 nm, where the main signatures of melting complete in a few picoseconds. Water ice melting after an ultrafast $T$ jump has been studied by time-resolved infrared spectra (13, 16), with a sample thickness of 1.6 μm and over a time window of 250 ps. Here, the spectral changes attributed by the authors to melting mostly occur in the first 150 ps after the pulse ($T = 37$ ps) (16). At 250 ps an incomplete melting was still observed, consistent with the amount of energy delivered.

The knowledge at this picosecond–nanometer scale barely connects to the experiences in the macroscopic world. On the macroscopic side, photographic investigations have been performed with millisecond resolution to investigate premelting structures in colloidal crystals (17), ice nucleation events upon cooling (18), or the rate and topology of ice and hydrate formation under dynamic compression (19, 20).

Here, we use a picosecond $T$-jump technique and time-resolved Mie scattering to explore the melting and the successive refreezing on bulk samples of ice I$_h$ and ice VI. The main peculiarities of this experiment are the bulk sample thickness (50 μm) and the time sampling: We access a time window of tens of milliseconds, which is the time needed to completely restore the initial conditions, with nanosecond resolution. We observe the scattering at ice/melt interfaces and the propagation of melting over distances of micrometers, accessing the characteristic time of the process. As will be shown, the $P$, $T$, and $V$ conditions in this experiment are quasi-static over the timescale of melting evolution. The kinetics of melting propagation in a bulk crystal are thus explored over the entire mesoscopic regime, connecting the microscopic and the macroscopic realms.

**Significance**

The complete unfolding of the melting process, from the nucleation onset to the achievement of a bulk liquid structure, is not known to date for the timescales and the sizes of the heterogeneities involved. Here, we observe in ice the archetypal H-bonded molecular crystal, the evolution of solid/liquid interfaces generated by the absorption of a picosecond infrared pulse. The pulse delivers all of the energy needed for complete melting; therefore, the lattice is homogenously heated from within, above its melting temperature. The growth of liquid domains over distances of micrometers takes hundreds of nanoseconds and is orders of magnitude slower than vibrational dynamics.

Author contributions: M.C., S.F., P.F., and R.B. designed research; M.C., S.F., and N.F. performed research; M.C., S.F., and N.F. analyzed data; and M.C. and R.B. wrote the paper. The authors declare no conflict of interest. This article is a PNAS Direct Submission.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1620039114/-/DCSupplemental.
The experimental insight into the melting dynamics of ices has paramount relevance in understanding natural phenomena and is a fundamental benchmark for theories at any level of accuracy. Ices, ubiquitous in terrestrial and extraterrestrial environments, are characterized by hydrogen-bond networks that determine the great complexity of their physical and chemical behavior. The melting line of water borders at least five crystalline phases (I_h, III, V, VI, and VII) with different structures and H-bond arrangements. In this work we investigate the melting dynamics in ice I_h and VI, accessed respectively by the use of low temperature and high static pressure, providing an unique experimental study in the mesoscopic domain and opening the way to investigations in different P and T conditions.

Results
Temperature Jump and Transient Transmission Loss. Ice I_h and ice VI samples 50 μm thick, at fixed temperature (T_0) and pressure (P_0), are “instantaneously” heated by a 15-ps pulse of light at 1.930 nm (FWHM = 100 nm) (21) with a focus diameter of 400 μm. Ice I_h at ambient pressure is held between fluo- rite windows in a cryostat at a static temperature T_0 ranging between 254.2 K and 272.6 K. Ice VI is in a sapphire anvil cell, between sapphire anvils, at room temperature and P_0 = 1.2 GPa or 1.4 GPa. The light is absorbed by the ice through excitation of a vibrational combination band (ν_1 + ν_2, ν_3 + ν_2), as shown in Fig. L4. The incident energy used (3–9 mJ/pulse) is well below the estimated ionization limit (9) and below the threshold of absorption saturation. In fact, the measured absorbance of the sample under irradiation with the pump is ~0.55 at all energies used. This low absorbance guarantees that the sample is uniformly irradiated along the beam axis and can thus be uniformly heated across its length. The pump causes an isochoric temperature jump (T-jump) up to ~400 K after the pulse, depending on the amount of delivered energy (Fig. 1B), and the formation of a superheated crystal at T_1 > T_m. This T-jump is achieved through redistribution of the vibrational energy through the lattice modes (thermalization), completed in ~20 ps, during which melting already starts (13, 16). The estimated pressure change (1.3 MPa K⁻¹) (13) is 50 MPa during the pulse and rapidly decreases due to melting itself in ice I_h (9). In this experiment, the energy absorbed in a single pulse exceeds that needed to heat the sample to T_m and to obtain its complete melting (E > 2 mJ for ice I_h and E > 3 mJ for ice VI; Physical Values Used in the Calculations).

The probe is a monochromatic continuous-wave laser beam (we used λ_probe = 405 nm, 457.9 nm, 632.8 nm, and 1,064 nm), with which we measure the transmission through the sample with a fast Si photodiode (Fig. 1C). The focus of the probe (~150 μm in diameter) lies inside the area irradiated by the pump. When a pump pulse is shot, the probe transmission drops to a minimum in tens or hundreds of nanoseconds, depending on the amount of deposited energy, and then returns to a static value in a time (micro- to milliseconds) strongly dependent on T_0. The transmission change is due to scattering at ice/melt interfaces, forming with the T-jump and evolving in time during melting (due to superheating) and refreezing (due to the thermal contact with the environment that decreases T to the thermal bath temperature T_b). When the transmitted beam is blocked (Fig. 1D), a positive signal due to off-axis scattered light is consistently observed, with a similar time dependence to that of the transmission change. In both configurations the signal amplitude increases as λ_probe decreases, as expected for scattering. As also expected, the transmission change is not observed when liquid samples are heated by the T-jump pulse, except at the highest E values (E ≥ 4.5 mJ) where a strong oscillation of the transmission is observed, likely due to the formation of vapor bubbles. Otherwise, the transmission of the liquid always remains ~5–10% higher than the static transmission of ice, and only a weak (compared with that observed in ice) transmission decrease, due to thermal lensing, is observed (Transmission of the Liquid after the T-jump and Fig. S1). The absence of signal from the liquid confirms that the signal observed in ice is not affected by unwanted contributions such as interferences between pump and probe light on the photodiode or optical effects on the cell windows. Thermoreflectance (22, 23) does not contribute to our signal because of the absence of highly reflecting interfaces, and its transient signal would, however, be concluded in ~1 ns. The transmission loss due to scattering at ice/water interfaces has been used to detect the freezing of water into ice VII under multiple-shock experiments (6, 24), using white light. Here, with monochromatic probes, we can estimate the size and concentration of the scattering domains evolving after the pulse. Several fresh samples were studied, to check the reproducibility. Each sample was used for many shots, and each shot probes a single melting/crystallization event in a crystal with slightly different quality. The evolution is monitored for all of the time necessary to recover the initial conditions, and the measurements are repeated at time intervals ≥2 s to allow complete recrystallization.

Complete melting, induced by an increase in transmission to the liquid value, was seldom observed despite delivering an excess of energy to achieve the process. Only by using the maximum energy values with 270 K < T_0 < 273 K, or piling up

Fig. 1. Experiment outline. (A) FTIR spectra of liquid water (room conditions), ice I_h (263 K), and ice VI (1.2 GPa) superimposed to the emission spectrum of the pump. (B) Estimate of the initial temperature T_i just after the pulse, for an ice I_h sample at initial temperature T_0 = 263 K. The upper and lower limits are ideal cases of no melting and complete melting, respectively, during the 15 ps of the pulse. (C and D) During the experiment the probe beam is collected in two possible configurations to detect the transmission plus the scattering at azimuthal angles 0 < θ < 1.5° (C) or the scattering at 2° < θ < 5° (D). Corresponding time-dependent signals are shown on the left for each configuration (acquired with E = 3.5 mJ, T_0 = 269 K, λ_probe = 633 nm).
T-jump pulses with a 1- to 5-Hz rate, did we observe the liquid transmission value.

**Analysis of the Time-Dependent Transmission Loss.** The transmission curves were transformed into absorbance, using as reference the initial transmission of the crystal (Fig. 2A). To understand the time evolution of the signal, we must note that after the pulse the sample’s temperature $T(t)$ decreases, due to the thermal contact with the external environment, until it reaches the initial value $T_0$. As we will see, the thermal conduction through the sample and the sample’s walls occurs in a longer timescale than the initial melting, occurring at quasi-constant temperature $T_1$. The relative magnitude of these two timescales depends on the external temperature $T_0$ and on the amount of energy absorbed $E$, which determines $T_1$ (Fig. 1B). In particular, $T_1$ affects both the rate of thermal diffusion ($\propto T(t) - T_0$) and the rate of melting, which we may expect to be kinetically driven by the superheating, thus having a rate $\propto e^{T(t) - T_m}$.

The first maximum of the $A(t)$ curves (Fig. 2A and B) appears for $E \geq 2.5$ mJ as a sharp peak followed by a fast decrease. For $E \geq 3.5$ mJ there is a second maximum at longer times. The curves are accurately fitted by a monoexponential growth in the initial 500–1,000 ns. The time range in which this exponential law well reproduces the curve depends on both $E$ and $T_0$, being the result of the characteristic times of the two competing phenomena described above: melting at $T \sim T_1$ and thermal conduction, the latter reducing the superheating and the melting rate. As can be seen in Fig. 2C, the monoexponential time constant $\tau_1$ decreases exponentially with $E$, as expected, and spans five orders of magnitude from 15,000 ns to 5 ns. This time constant thus represents the characteristic times of melt growth, driven by the superheating of the crystal. For ice I$_h$, where many measurements were performed as a function of $T_0$, we find that $\tau_1$ and $A_1$ are independent of $T_0$ for $E \geq 2.5$ mJ, confirming that the thermal conduction is not relevant in the first 500–600 ns in the $T_0$ range probed (Effect of Thermal Conduction on the Melting Rate and Fig. S2).

The values of $\tau_1$ are the same for ice I$_h$ and ice VI within error bars, which represent the shot-to-shot repeatability of the scattering signal. The two ices have different crystal structures and different volume changes upon melting. Our measurements suggest, however, that the differences in the growth of the melt particles are very similar in the two ices. In the time range investigated ($t > 1$ ns) as we discuss in the next section, we have no access to the nucleation dynamics, where probably the largest difference between the two ices would appear.

**Size Evolution of Molten Domains**

**Calibration of our Setup and Determination of the Size of the Molten Particles.** To assess our experimental sensitivity to Mie scattering, we used the configuration of Fig. 1C, with the $T$ jump off, to measure the transmission through monodisperse suspensions of SiO$_2$ nanoparticles in water with diameters $D = 20$ nm, 80 nm, 200 nm, and 400 nm and different concentrations (C), in a quartz cuvette with optical path 10 mm or 0.1 mm (Calibration of the Detection Sensitivity and Fig. S3). The expected transmission loss (reported as absorbance) of each suspension was calculated as $A = C_{\text{geo}} \times C + h$, where $C$ is the particle’s concentration, $h$ is the thickness of the sample, and the Mie scattering cross-section $C_{\text{geo}}$ is computed using a FORTRAN code based on the program reported by Bohren and Huffman for monodisperse suspensions of spherical scatterers (25). The input also contains the wavelength $\lambda_{\text{probe}}$ of the probe light, the complex refractive indexes of the particles and surrounding medium, the diameter $D$ of the particles, and the range of azimuthal angles $\theta$ with respect to the forward direction (Fig. 1C and D) at which the light is collected. The output contains the matrix elements of the scattering cross-section for the single particles, from which the angular distribution of scattered light (for polarized or unpolarized light) can be calculated. The angular distribution of the scattered light is a property of the single particle and does not depend on the concentration and can thus be used to estimate $D$ for a monodisperse suspension. As shown in Fig. S3, the absorbance values measured on the calibration suspensions are in perfect agreement with those expected by the Mie-scattering theory. For $h = 0.1$ mm (twice that of our samples) the setup is sensitive to particle sizes down to $D = 200$ nm if $C \geq 1$ nm$^{-3}$. For one suspension ($D = 400$ nm, $C = 0.01273$ nm$^{-3}$ with $\lambda_{\text{probe}} = 632.8$ nm and $h = 10$ mm) we measured the signal in both configurations of Fig. 1C and D with the pump off. The ratio of the two signals, which is due to the angular distribution of the scattered light, yields an estimate of the scatterer’s diameter $D = 409$ nm. This result indicates that we are able, with the ratio of the signals in the two configurations, to correctly estimate $D$ for a monodisperse suspension.

For ice I$_h$ at $T_0 = 269$ K, using $E = 3.5$ mJ and $\lambda_{\text{probe}} = 632.8$ nm, transmission curves were measured in the two configurations of Fig. 1C and D after $T$-jump pulses as a function of time. In the simplest hypothesis that all of the scattering domains are approximately spheres with the same diameter $D$, the ratio between the two curves gives an estimate of $D$ (as discussed above) as a function of time. This diameter monotonically increases up to $\sim 1.5$ $\mu$m in 2.3 ms and then decreases (Fig. 3).

![Fig. 2.](https://example.com/fig2.jpg) **Analysis of the experimental curves at short delays.** (A, Upper) The transmission curve is transformed into absorbance using the static transmission $I_0$ as reference. (A, Lower) Example of exponential fit up to the first maximum $A_1$. (B) Absorbance curves obtained using different pump energies. (B, Lower) Zoom-in of the same curves in the range 0–2.5 $\mu$s. (C) Average $A_1$ and $\tau_1$ parameters resulting from the fit. The values are averaged over $\geq 10$ pulses, and for ice I$_h$ different $T_0$ conditions are included. The error bars represent the standard deviations.
The idealized spherical scatterers in the sample are thus identifiable as molten domains that grow and evolve until \( T > T_m \) and decrease during refreezing when \( T = T_m \). The estimation of their dimensions with this method is limited to large delays (\( t < 0.3 \text{ ms} \)) because the configuration of Fig. 1D is affected by a strong reflection of the pump beam. Also, it makes use of data from two different pulses, meaning two different ice samples, and of a weak off-axis scattering signal. Thus, the \( D(t) \) values obtained with this method are quite approximate but are useful to get an overall insight into our system.

**Model of the Melting and Refreezing Sample.** The simplest model capable of describing our heated sample and its evolution after excitation takes as the starting point the sample at \( T = T_0 \) after the \( T \) jump (the minimum delay experimentally accessed) as an already nucleated monodisperse suspension of water spheres randomly positioned in an ice matrix at homogenous temperature \( T_1 \), with initial diameter \( D_1 \) and initial concentration \( C_1 \). \( T_1 \) is set to 360 K (Fig. 1B); \( D_1 = 25 \text{ nm} \), as estimated in refs. 13 and 16; and \( C_1 \) is set to a different value for each simulation, ranging between 0.1 \( \mu \text{m}^{-3} \) and 5 \( \mu \text{m}^{-3} \). In the simulation (Simulation Details) we impose that the temperature at the sample's wall \( T \) decreases in time to the final value \( T_0 \) with an exponential law. The drops are set to grow, at each time step, all by the same amount, depending on \( T - T_0 \), and coalesce when they touch each other. When \( T < T_m \), the drops decrease instead of growing. At all time steps, the absorbance is calculated on a monodisperse suspension where all of the drops have the average diameter. The rate constants for the temperature decrease, drops' growth, and drops' decrease are chosen to reproduce the shape of the curve. The simulation does not provide any indication on the actual timescales of the processes, which are derived only by the experiment. The simulation is essential to validate the approximations made. In fact, despite its simplicity and the simulation box being quite small (\( 10 \times 10 \times 10 \text{ nm}^3 \)), it is able to reproduce with great detail the experimental curves, as can be seen by comparing Figs. 2 and 4. In particular, the effect of increasing \( C_1 \) reproduces perfectly the effect experimentally observed by increasing \( E \) (Figs. 2B and 4B). When \( C_1 \) is sufficiently large, a critical diameter is reached for which a catastrophic coalescence occurs, and the resulting \( A(t) \) curve has a sharp maximum \( (A_1) \). By further increasing \( C_1 \) a second maximum due to large drops formation appears. This behavior confirms that \( E \), as expected, by determining the initial temperature after the \( T \) jump \( (T_1) \) also determines the initial concentration of melting nuclei. The saturation of \( A_1 \) with \( E \) (Fig. 2C) likely indicates a limit superheating temperature, previously estimated as \( \sim 330 \text{ K} \) (13, 26), above which the number of melting nuclei becomes independent of \( T \).

The model allows us to constrain the scatterers' concentration \( C \) and obtain an estimate for their diameters \( D \), in the approximation of the sample as a monodisperse suspension of water spheres in ice (Fig. 5A). In fact, the simulation shows that \( C \) is approximately constant before the catastrophic coalescence, occurring at a time \( t_C \) where the sharp maximum is observed. During coalescence \( (t \geq t_C) \) \( C \) and \( D \) can be linked by a packing constraint, such as the simple cubic \( C = 1/D^3 \). We thus obtain, for the \( A(t) \) curves measured with \( E = 3.5 \text{ mJ} \), \( D = 430 \pm 15 \text{ nm} \) and \( C = 13 \mu \text{m}^{-3} \) at \( t_C \sim 200 \text{ ns} \) (Fig. 5B), with very good agreement among the \( \Lambda_{\text{probe}} \) values (Size of the Molten Regions Versus Time and Fig. S4). Moreover, imposing that the concentration is constant at \( C(t) = C(t_C) \) for \( 0 < t < t_C \), we can deduce \( D(t) \) at \( t < 200 \text{ ns} \) (Fig. S4). As shown in Fig. 5B, the melt domains grow slowly in time, from \( \sim 200 \text{ nm} \) to \( \sim 400 \text{ nm} \) in \( \sim 200 \text{ ns} \). The refreezing starts when the temperature of the sample's wall, in contact with the environment, has reached \( T_m = 273 \text{ K} \). During freezing, heat is constantly removed by the thermal bath, whereas we can assume that the sample remains at \( T_m \). Thus, the freezing rate should be dependent on the rate of heat diffusion through the ice/water system to the cell walls, proportional to \( T_m - T_0 \). To investigate the refreezing rate, we analyzed \( A(t) \) curves obtained in the \( I_0 \) with \( E = 2.5 \text{ mJ} \) and \( \Lambda_{\text{probe}} = 632.8 \text{ nm} \), in a series of measurements at different \( T_0 \) conditions. The decreasing part of the \( A(t) \) curves was fitted to an exponential decay. To relate this decay to the sample's state, we estimated here an average diameter \( D(t) \) of the molten domains, decreasing with time, assuming \( C \) constant in this time range, at a value \( C_2 \). This value is obtained by imposing the packing constraint \( C_2 = 1/D_2^3 \), where \( D_2 \) is the maximum diameter of the drops (1,500 nm) obtained from the analysis of the angular distribution (Fig. 3). The resulting \( V(t) = \pi D(t)^3/6 \) curves are well fitted to an exponential decay. As expected, the rate constant \( 1/\tau \) increases linearly with \( T_0 - T_m \) (Fig. 5C).

**Conclusions**

Time-resolved Mie scattering has been successfully used to monitor the melting and the successive recrystallization of water ices \( I_0 \) and VI with a nanosecond time resolution. The melting is induced by an ultrashort IR pulse resonant with a vibrational combination band and its dynamics are probed from a few
nanoseconds after the heating pulse, not having therefore access to the nucleation of the melt seeds. The latter form after the fast relaxation of the absorbed energy (tens of picoseconds) at hotspots created by or localized around absorbing molecules. The entire growth dynamics of these melting seeds, from a few nanoseconds to tens of milliseconds, are monitored in the mesoscopic regime up to the successive and complete recrystallization. The experimental data, including the most peculiar features, are excellently reproduced by a simple phenomenological model in which a monodisperse distribution of liquid spherical particles grows, rearranges during coalescence, and decreases its volume when the temperature reaches again the melting temperature. Despite the strong approximations used (nucleation law, shape and size homogeneity) we are able to provide a precise time evolution of the droplets’ dimensions that nicely connects the previous knowledge of the initial 250 ps (9, 13, 16, 27) to the macroscopic domain. The melting implies the relaxation of the superheated lattice at ice/water interfaces. However, the temperature at these interfaces decreases in time due to melting itself, which is endothermic, and thus the growth slows down as it proceeds, as also reproduced in calculations for the subnanosecond time window (9). The heat exchange with the environment also contributes to slowing down the growth by decreasing the sample’s temperature and eventually reverses the process; however, this has a much slower rate (micro- to milliseconds) and for \( E > 2 \, \text{mJ} \) does not affect the sample’s behavior in the initial microseconds as demonstrated by the independency of \( T_m \) on \( T_0 \). Thus, in this timescale (1 ns–1 µs) the relevant dynamics are those of the lattice relaxation to its equilibrium liquid structure at \( T > T_m \). For our sensitivity, ice \( I_0 \) and ice VI melt with the same dynamics in the 1-ns to 1-µs time range. The specific arrangement of the crystal structure is more likely related to the nucleation kinetics, which are not accessed here. We have thus unveiled fundamental aspects of the dynamics of melting of water ices, in a time domain previously unexplored. The phase transitions of water rule many natural phenomena. Moreover, water is the archetypal H-bonded system and is a benchmark for theory and simulations that can take advantage of this knowledge in the mesoscopic domain and in a time scale inaccessible to many computational methods. The experimental approach used in this work paves the way to a plethora of dynamic studies concerning the formation and growth of heterogeneities in bulk materials, including solid-state reactivity and formation of clathrate hydrates, topics of current great interest for understanding the processes at the Earth’s interior.

**Materials and Methods**

Ice \( I_0 \) and ice VI are prepared using water from Aldrich, HPLC grade, filtered with MillexLV Durapore PVDF syringe filters (pore size 0.1 \( \mu \)m). For \( I_0 \), the water is loaded in a room-pressure cell with \( \text{CaF}_2 \) windows and a polytetrafluoroethylene (Teflon) spacer with 50 \( \mu \)m thickness and 25.4 mm diameter, which is inserted in a Peltier cryostat and cooled to 250 K. The temperature is then increased to the desired \( T_0 \) value (254.2–272.6 K). For ice VI, liquid water is loaded in a membrane sapphire anvil cell (Melles Griot 25-LHR-691) equipped with \( z \)-cut, low fluorescence sapphire anvils (Almax EasyLab) and a copper-beryllium gasket. The sample is 50 \( \mu \)m in thickness and 500 \( \mu \)m in diameter. The sample is compressed to 1.5 GPa at room temperature, and then the pressure is lowered to the desired \( T_0 \) value (1.2 GPa or 1.4 GPa). The fluorescence of a ruby chip 5 \( \mu \)m in diameter is used as a pressure gauge (28). The presence of ice VI in the SAC is checked by measuring the FTIR spectrum with a Bruker spectrometer IFS120 HR (29).

The \( T \)-jump source, described in ref. 21, is an optical parametric generator and amplifier pumped by a mode-locked Nd:Yag laser (EKSPLA PL2143 A; 20-ps pulses, maximum energy 55 mJ/pulse, maximum repetition rate 10 Hz). The source produces 15-ps pulses tunable in the range 1,700–2,300 nm (FWHM = 100 nm), with a maximum efficiency at 1,930 nm where it can provide up to 15 mJ/pulse. The pulse at 1,930 nm is focused to have an irradiated diameter of \( \sim 400 \mu \)m. The absorbance of the sample under irradiation with the \( T \)-jump source was determined by measuring the transmission with a pyroelectric energy meter (Gentec-Eo QE25LP-S-M8), using as reference the empty cell. The absorbance is 0.55 ± 0.30 for both types of sample and is constant in all of the \( T \)-jump energy ranges used, indicating that saturation of absorption is not reached even at the highest \( T \)-jump energy. The energy needed to heat the irradiated volume by 1 K is 11.5 \( \mu \)J for ice \( I_0 \) and 22.6 \( \mu \)J for ice VI (30, 31). The energy needed to completely melt the irradiated volume at the melting point is 1.92 mJ for ice \( I_0 \) and 2.90 mJ for ice VI (32). Thus, the energy absorbed by the ice in a single pulse is sufficient to completely melt the irradiated volume and heat it of some tens of kelvins. The probe lasers are as follows: a laser diode, Thorlabs CPS 405 (405 nm); an Ar” laser, Coherent Surelite 90 (457.9 nm); a He-Ne laser, Melles Griot 52-5-LHR-691 (632.8 nm); and an Nd:YAG laser, Lightwave 126 (1,064 nm), with \( \sim 5–10 \) mW on the sample. The independence of the transmission on the probe power was always verified. The probe laser is focused on the sample to a focus diameter of \( \sim 150 \mu \)m, and the transmission (Fig. 1C) or scattering (Fig. 1D) is collected and focused on a UV-enhanced Si photodiode with cutoff frequency \( f_c = 60 \) MHz (Hamamatsu S1722-02) or an APD photodiode with \( f_c = 3 \) GHz (First Sensors). For transmission (configuration of Fig. 1C) a diaphragm with aperture 2–8 mm (depending on the spatial shape and divergence of the probe beam) is placed close to the lens to collect light at a small angle (0 < \( \theta < 1.5^\circ \)). For scattering (configuration of Fig. 1D) the diaphragm is removed, a beam stopper is placed to stop the directly transmitted beam, and the scattered light is collected in the whole angle (2 < \( \theta < 7^\circ \)) accepted by the collecting lens (25.4 mm in diameter). The photodiode signal is monitored and recorded on a Rohde- Schwarz 2-GHz oscilloscope (R5 RT1024). The scattering signal as in Fig. 1D was measured only in ice \( I_0 \), at \( T_0 = 269 \) K and \( E = 3.5 \) mJ (energy absorbed by the sample). After each pump pulse, we can see by eye a different speckle produced by the static scattering of the probe beam by the sample, consistent with melting and refreezing. Window materials with different thermal conductivity (sapphire and fluorite) were used on ice \( I_0 \) to check whether thermal diffusion through their surface could be the rate-limiting process. The results are independent of the window’s material, consistent with thermal diffusion in ice/water (thermal conductivity: \( k \sim 0.6 \text{ W K}^{-1} \text{ m}^{-1} \) for water, \( k \sim 2.2 \text{ W K}^{-1} \text{ m}^{-1} \) for ice) being slower than through the
windows (k \sim 9 \text{ WK}^{-1} \text{m}^{-1} \text{ for CaF}_2, k \sim 25 \text{ WK}^{-1} \text{m}^{-1} \text{ for sapphire}) or at the windows/sample interfaces (values for interfacial thermal resistance not available).

**ACKNOWLEDGMENTS.** This work was supported by the Deep Carbon Observatory initiative (Extreme Physics and Chemistry of Carbon: Forms, Transformations, and Movements in Planetary Interiors, from the Alfred P. Sloan Foundation), by the Grant Futuro in Ricerca 2010 RBFR1092HQ funded by the Italian Ministero dell’Istruzione, Università, Ricerca under the program Fondo Italiano per la Ricerca di Base (FIRB); and Fondazione Cassa di Risparmio di Firenze under the project “Chimica Ultraveloce ad Altissima Pressione.”