respectively. Thus on compression, $\beta$-Si$_3$N$_4$ will directly transform to c-Si$_3$N$_4$ and not to the hypothetical w-Si$_3$N$_4$ with lower density. This finding agrees with our synthesis of c-Si$_3$N$_4$ above 15 GPa.

The structural parameters for the optimized geometry of c-Si$_3$N$_4$ are $a = 7.76 \text{ Å}$ and $\beta = 0.0074$. Fitting a Murnaghan equation of state to the calculated $E$–$V$ data we obtained a bulk modulus of 300 GPa. This is about 20–30% higher than the experimental values reported for $\alpha$-Si$_3$N$_4$ (229 GPa; ref. 13) and $\beta$-Si$_3$N$_4$ (250 GPa; ref. 24). Our calculations of the bulk moduli of the $\alpha$- and $\beta$-phase gave 227 GPa and 249 GPa, respectively. Furthermore, we calculated the shear modulus $\mu_a$ to be 340 GPa for c-Si$_3$N$_4$ and 150 GPa for $\beta$-Si$_3$N$_4$.

The calculated bulk and shear $\epsilon_{44}$ moduli for c-Si$_3$N$_4$ are close to that of stishovite, a high-pressure phase of SiO$_2$ where the silicon atoms are octahedrally coordinated to oxygen. The high coordination leads to a significant increase in density (4.29 g cm$^{-3}$; ref. 4), bulk modulus (281–313 GPa; ref. 25) and $\epsilon_{44}$ modulus (252 GPa; ref. 26) with respect to the low-pressure modifications of SiO$_2$ (such as quartz). Moreover, it was found recently that the hardness of SiO$_2$-stishovite exceeds that of any other known oxide (Knoop hardness 33 GPa; ref. 3). Because the compressibility and the $\epsilon_{44}$ modulus of $\beta$-Si$_3$N$_4$ and SiO$_2$-stishovite are of comparable magnitude we expect that the hardness of c-Si$_3$N$_4$ will be close to that of stishovite which is considered to be the third hardest material after diamond and cubic BN (ref. 3). Because of this, and of its metastability in air at ambient pressure and high temperatures, c-Si$_3$N$_4$ can be considered for technological applications.

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Methods
We calculated the total energies within the local-density approximation (LDA) and the generalized gradient approximation (GGA) of the exchange and corelation energy with standard plane-wave ($E_{\text{xc}} = 70 \text{ Ry}$) pseudopotential techniques. Special $k$-points (10 for c-Si$_3$N$_4$ and w-Si$_3$N$_4$, 15 for $\beta$-Si$_3$N$_4$) were used to integrate over the Brillouin zone. At a given volume, the atomic positions were relaxed and in addition for $\beta$-Si$_3$N$_4$ the c/a ratio was optimized. A detailed description of the method, further calculations and discussions, including differences in results between the LDA or GGA, will be presented elsewhere.

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Extending the methodology of X-ray crystallography to allow imaging of micrometre-sized non-crystalline specimens

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The contrast and penetrating power afforded by soft X-rays when they interact with matter makes this form of radiation ideal for studying micrometre-sized objects. But although soft X-rays are useful for probing detail too fine for visible light microscopy in specimens too thick for electron microscopy, the highest-resolution applications of X-ray imaging have been traditionally limited to crystalline samples. Here we demonstrate imaging (at ~75 nm resolution) of a non-crystalline sample, consisting of an array of gold dots, by measuring the soft X-ray diffraction pattern from which an image can be reconstructed. The crystallographic phase problem—the usually unavoidable loss of phase information in the diffraction intensity—is overcome by oversampling the diffraction pattern, and the image is obtained using an iterative algorithm. Our X-ray microscopy technique requires no high-resolution X-ray optical elements or detectors. We believe that resolutions of 10–20 nm should be achievable; this would provide an imaging resolution about 100 times lower than that attainable with conventional X-ray crystallography, but our method is applicable to structures roughly 100 times larger. This latter feature may facilitate the imaging of small whole cells or large subcellular structures in cell biology.

When an object is illuminated by a plane wave, the amplitude of the far-field diffraction pattern is the Fourier transform of the object. The microscope typically uses a lens to perform the inverse transform to create the image. The resolution of a perfect lens is limited by diffraction to $d > 0.61 \lambda /NA$, where $\lambda$ is the wavelength and NA is the numerical aperture of the lens. For the visible region of the spectrum, there are high-NA lenses which provide imaging near the limit set by the wavelength, and further improvements are possible using confocal and video techniques.

To get to considerably higher resolution, microscopists use shorter wavelengths, such as are obtained from electrons and X-rays. Transmission electron microscopes routinely image specimens up to ~0.5 mm thick, whereas X-ray microscopes are particularly useful for somewhat thicker specimens which may also be wet.

The resolution of X-ray microscopes has been limited by the available optical elements (‘optics’) to about 30–50 nm (refs 8, 9), and for three-dimensional imaging to about 100–1000 nm (refs 10–12) or,
in Gabor holography, by the resolution of the detector and/or the optics\textsuperscript{13,14}.

X-ray crystallography is widely used for very-high-resolution imaging of molecular structure, when these molecules are arranged in a regular crystalline array. This technique requires no optics, and does not impose stringent resolution requirements on the detector. The multiple copies of the specimen amplify the signal, and their regular arrangement concentrates the far-field diffraction pattern into discrete Bragg peaks.

That the general approach of crystallography could be extended to image non-crystalline specimens was first proposed by Sayre in 1980\textsuperscript{15}. This approach, although it poses particular challenges in recording and reconstructing the diffraction pattern\textsuperscript{16}, has the potential to extend the resolution of three-dimensional X-ray microscopy beyond the technical limitations mentioned above, through extending the class of structures to which the powerful techniques of X-ray crystallography can be applied. Here we report the first (to our knowledge) successful recording and reconstruction of such an X-ray diffraction pattern.

The specimen was a collection of gold dots, each \(\sim 100\) nm in diameter and \(80\) nm thick, deposited on a \(100\)-nm-thick silicon nitride membrane, to form a set of six letters (Fig. 1). This specimen was illuminated with \(\lambda = 1.7\) nm monochromatic and parallel X-rays from the X1A undulator beamline at the National Synchrotron Light Source. To ensure spatial coherence of the illumination, a \(10\)-\(\mu\)m-diameter pinhole was placed at a distance of 2.5 cm upstream of the specimen. To limit the effect of the scatter from the edge of this pinhole, the specimen was placed only \(\sim 30\) \(\mu\)m from the corners of the silicon nitride membrane, allowing the silicon support to protect three quadrants of the detector from the scatter. In addition, the pinhole served to reduce the size of beam-stop needed to protect the detector from the direct beam; a \(220\)-\(\mu\)m-diameter wire placed in front of the detector was used as beam stop. The detector—a back-thinned, liquid-nitrogen-cooled CCD with \(512 \times 512\) pixels and a \(24\) \(\mu\)m \(\times 24\) \(\mu\)m pixel size—was placed downstream of the specimen at a distance of 25 cm. A photodiode could be inserted between the beam stop and the CCD to monitor the beam intensity in the presence or absence of pinhole, beam stop and specimen, and to help align these components in the beam. The apparatus was in vacuum with an air-lock for rapid sample change. A typical diffraction pattern is shown in Fig. 2, in which the fourth-quadrant data were obtained by using central symmetry. Since the central region was obscured by the beam stop, we replaced the central area of the X-ray diffraction pattern by a patch from the squared magnitude of the Fourier transform of an optical microscope image (Fig. 3). The patch is a circular area with a 15-pixel radius, which occupies less than 0.5% of the whole diffraction pattern. The exposure time of the pattern was 15 min which corresponds to an incident flux of \(1.65 \times 10^{19}\) photons \(\text{m}^{-2}\), or a radiation dose of \(1.56 \times 10^6\) gray (Gy) to the specimen. The pattern extends to the edge of the CCD, suggesting that a larger detector would directly lead to higher spatial resolution.

The intensity of the diffraction pattern provides a record of the size, but not the phase, of the diffraction amplitude. To reconstruct the image, one faces therefore the ‘phase problem’ of crystallography. The situation for the non-crystalline specimen is different, however, in that the pattern is continuous rather than limited to
Forcing of the cold event of 8,200 years ago by catastrophic drainage of Laurentide lakes


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The sensitivity of oceanic thermohaline circulation to freshwater perturbations is a critical issue for understanding abrupt climate change. Abrupt climate fluctuations that occurred during both Holocene and Late Pleistocene times have been linked to changes in ocean circulation4,5, but their causes remain uncertain. One of the largest such events in the Holocene occurred between 8,400 and 8,000 calendar years ago2,7,8 (7,650–7,200 14C years ago), when the temperature dropped by 4–8°C in central Greenland2,13 and 1.5–3°C at marine sites and terrestrial sites around the northeastern Atlantic Ocean. The pattern of cooling implies that heat transfer from the ocean to the atmosphere was reduced in the North Atlantic. Here we argue that this cooling event was forced by a massive outflow of fresh water from the Hudson Strait. This conclusion is based on our estimates of the marine 14C reservoir for Hudson Bay which, in combination with other regional data, indicate that the glacial lakes Agassiz and Ojibway9–11 (originally dammed by a remnant of the Laurentide ice sheet) drained catastrophically 8,470 calendar years ago; this would have released >1014 m3 of fresh water into the Labrador Sea. This finding supports the hypothesis2,8,14 that a sudden increase in freshwater flux from the waning Laurentide ice sheet reduced sea surface salinity and altered ocean circulation, thereby initiating the most abrupt and widespread cold event to have occurred in the past 10,000 years.

During the period of deglaciation that preceded the abrupt climate event of 8,400–8,000 calendar years ago (the ‘8.2-kyr event’), a remnant Laurentide ice mass occupied Hudson Bay and served as an ice dam for glacial lakes Agassiz and Ojibway9–12 (Fig. 1). The rapid collapse of ice in Hudson Bay allowed lakes Agassiz and Ojibway, which had previously discharged over spillways southwards to the St Lawrence estuary, to drain swiftly northwards through the Hudson Strait to the Labrador Sea15,16.