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The sixteenth century Alderney crystal: a calcite as an efficient reference optical compass?

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The crystal recently discovered in the 1592 sunken Elizabethan ship is shown to be an Iceland spar. We report that two main phenomena, with opposite effects, explain the good conservation and the evolution of this relatively fragile calcite crystal. We demonstrate that the Ca^{2+} – Mg^{2+} ion exchanges in such a crystal immersed in sea water play a crucial role by limiting the solubility, strengthening the mechanical properties of the calcite, while the sand abrasion alters the crystal by inducing roughness of its surface. Although both phenomena have reduced the transparency of the Alderney calcite crystal, we demonstrate that Alderney-like crystals could really have been used as an accurate optical sun compass as an aid to ancient navigation, when the Sun was hidden by clouds or below the horizon. To avoid the possibility of large magnetic errors, not understood before 1600, an optical compass could have helped in providing the sailors with an absolute reference. An Alderney-like crystal permits the observer to follow the azimuth of the Sun, far below the horizon, with an accuracy as great as $\pm 1^\circ$. The evolution of the Alderney crystal lends hope for identifying other calcite crystals in Viking shipwrecks, burials or settlements.

1. Introduction

Although crystals used as sun optical compass are mentioned in the saga of Saint Olaf [1] relating to the Viking navigation around the tenth century, no Viking sunstones had yet been discovered, and particularly, none in any way connected with an actual ship. Such crystals are supposed to help the sailors to locate the Sun using the polarization pattern of the sky [2–6] when it is hidden by clouds or below the horizon [3,7–12]. Recently, a first crystal incontrovertibly associated with a ship has been found, near a pair of navigation dividers, by one of us (S.W.) on the site of a sixteenth-century shipwreck, the Alderney Elizabethan shipwreck [9,13]. After the defeat of the Spanish Armada in 1588, Queen Elizabeth I sent ships full of weapons to Brittany (to Granville and Saint-Malo harbours). The ship went down off the coast of Alderney in 1592 [14], i.e. about five centuries after the Viking age and the Viking navigation towards America, but however more than two centuries before the discovery of the polarization of the light in optics [15]. Of course the introduction of the magnetic compass in Europe, about the thirteenth century, brought a major change in navigation. However, although the magnetic compass became widely used, no one understood exactly why it worked until the experiments of Gilbert at the end of the sixteenth century [16,17]. In particular, the complex and mysterious geographical variations, the uncontrolled magnetic perturbations and the deviations of the magnetic needle remained unexplained. Although it seems there is no reference to sunstones in the post-Viking navigation literature, they are however mentioned in the inventories of churches and cloisters in the fourteenth and fifteenth centuries, existing as physical objects but without discussing their attributes or their derivations [18]. Consequently, one may wonder if the presence of such a crystal on board, a ship in the sixteenth century could still possibly be of any use for navigation and if it could bring new insights for the search for crystals of the Viking Age. After confirming chemically that the excavated Alderney crystal is an Iceland spar, i.e. a calcite crystal, we have to try to understand its chemical evolution, its mechanical conservation and the optical potential of an Alderney-like crystal.

2. Material and methods

(a) Material

The Alderney crystal excavated from the site of an Elizabethan shipwreck has remained for more than 400 years in sea waters and sand, off the coast of Alderney, subjected to very strong currents. The crystal and many other items associated with the Elizabethan ship, survived in an underwater cove where sand accumulated and provided protection. In spite of the challenging conditions, the crystal shown in figure 1a has kept a perfect rhombohedral geometry and measures $5 \times 3 \times 2.4$ cm. The 102° obtuse angle and the 78° acute angle are exactly the same as those of similar cleaved calcite crystals, similar to the one shown in figure 1b. However, the calcite crystals (calcium carbonate, CaCO_3) are rather fragile as calcite is no. 3 on the Mohs hardness scale. Figure 1a shows that the crystal transparency has decreased during its long stay in sea water and sand, compared with that of the Alderney-like crystal shown in figure 1b.

(b) Methods

To confirm the chemical composition of the Alderney crystal and to understand its conservation and evolution in sea water, we have carried out inductively coupled plasma-atom emission spectroscopy (ICP-AES) tests using a Thermo Scientific iCAP spectrometer. This technique permits the identification of the different elements in the bulk of any crystal and the measurement of their respective concentrations. The spectrometer is well adapted to detect the main expected element, i.e. calcium, but also magnesium and sodium, the most common ions found in sea waters. In this technique, the Ca^{2+} and Mg^{2+} ions are excited by a plasma and respond at the wavelengths 317.9 and 279.5 nm, respectively. A few milligrams are sufficient to realize a

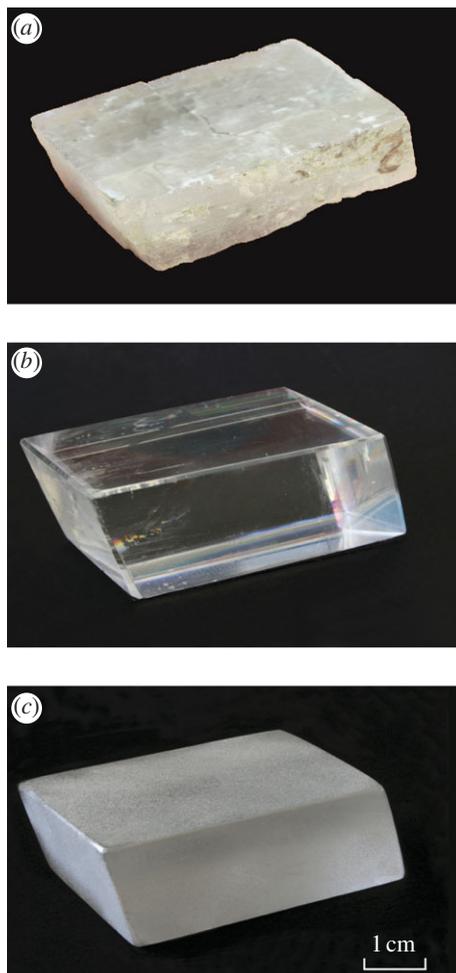


Figure 1. (a) The Alderney crystal ($5 \times 3 \times 2.3$ cm). After more than 400 years immersion in the Channel sea water, the rhombohedral geometry is unchanged, but the transparency is reduced. (b) Similar Brazilian crystal ($5 \times 3 \times 2.5$ cm). The transparency of this Alderney-like is quasi-perfect. (c) The same crystal after sand abrasion and a two-week immersion in Channel sea water. The Mie scattering and the Mg^{2+} – Ca^{2+} exchanges on the surface have reduced its transparency. (Online version in colour.)

quantitative bulk analysis for each crystal. Additional chemical laboratory tests allow us to investigate the specific interaction of different ions with virgin calcite crystal surface. Indeed, when a cleaved calcite crystal is partially immersed in water solutions containing either Mg^{2+} or Na^+ ions for only some weeks, the electron microscope (JEOL 6400) associated with an energy-dispersive X-ray spectrometer is able to identify and measure quantitatively the induced chemical changes on the crystal surface. By simply comparing the results obtained for the immersed and the non-immersed parts of the crystal, we get a precise differential signature.

Mechanical sand abrasion tests are carried out using silica with a commercial sand blaster. The roughness analyses are performed using a Taylor-Hobson surface contact profilometer. To assess the hardness of the calcite crystals, we test different thermal techniques, namely by heating the crystals at different temperatures in an oven. To estimate the possible spurious magnetic deviations on board the Alderney ship full of weapons, we have moved a magnetic compass near the different metallic artefacts excavated from the ship on display at the Alderney Museum, namely near one of the excavated cannons.

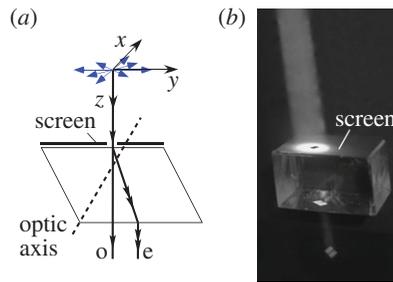


Figure 2. Case of an unpolarized light impinging on a calcite crystal. (a) Scheme; unpolarized light. (b) Unpolarized sun beam. Photo showing the two images with equal intensities whatever the crystal orientation. (Online version in colour.)

To evaluate the optical potential of an Alderney-like crystal, we extend the differential method using ordinary and extraordinary beams [12] so as to introduce the different possible working points. Such a crystal equipped with an opaque screen with a small square hole (figure 2a) produces two narrow beams at the output, as shown in figure 2b, the ordinary and extraordinary beams being separated by the walk-off distance of about 2.4 mm for this Alderney-like crystal. For an incident unpolarized beam, similar to the one used by Bartholin, who first discovered the ordinary and extraordinary beams in an Iceland spar, the two images have equal luminosities whatever the orientation of the crystal (see the translation: [19]). By contrast, using an incident linearly polarized light as in figure 3, the well-known Malus' response [20] through a perfect polarizer when the polarizer is rotated, is shown in figure 3a. The usual working point used to determine the polarization axis of the light with a polarizer, corresponds to $\alpha = 90^\circ$ for the so-called crossed-polarizer orientation, where α is the angle between the polarization of the incident light and the passing axis of the polarizer. Note that the derivative of the transmission function shows a zero value for $\alpha = 90^\circ$ as shown in figure 3a, leading to a too low sensitivity of any method using a polarizer [21]. However, if for a depolarizer the working point is located at $\alpha = 45^\circ$, the incident polarization of the light is also at 45° from the optic axis of the calcite in this case, and then the intensity variations are maximized as the derivative is equal to 1 around this working point, as shown in figure 3a. So the contrast between the ordinary and extraordinary beam intensities $\Delta I/I = |I_o - I_e|/(I_o + I_e)$ will exhibit sharp variations on both sides of this working point as shown in figure 3b. Now, when we compare quantitatively the efficiency of the polarizer and that of the depolarizer methods around their 90° and 45° working points, respectively, we can see in figure 3c that the detection signal is more than 10 times larger for the birefringent crystal than for the best dichroic polarizer. Of course, as noted above, for the depolarizer the working point at 45° is fixed by its optic axis and in no case by the edges of the crystal as done by Ramskou and Karlsen [1,7,9,10], who considered the calcite as a polarizer. Namely, fixing a pointer for the Sun bearing along one of the two edges of the crystal have led Ramskou and Karlsen to a $+6^\circ$ error for the pointer along one edge, and a -6° error for the pointer along the other edge. For an Alderney-like crystal equipped with a screen as in figure 2, applying twice the Malus' law for the ordinary and the extraordinary beams around the 45° isotropy point as a working point, the normalized difference of irradiances of the two images can be written as $\Delta I/I = |I_o - I_e|/(I_o + I_e) = \rho |\cos 2\alpha|$, where α is the angle between the ordinary axis of the crystal and the main axis of the partially polarized light. Here, ρ is the degree of polarization of the incident light and is defined by $\rho = (I_{\max} - I_{\min})/(I_{\max} + I_{\min})$ [20], where I_{\max} and I_{\min} are the maximum and minimum intensities, respectively, measured through a usual polarizer (figure 4a). The theoretical V-shaped curves associated with the differential method are shown in figure 4b for the different values of the degree of polarization of skylight encountered for instance at the English Channel latitudes. As the human eye is able to appreciate contrast as low as 0.01 [22], we note that the polarization observations can be made for many types of situations. For instance, for $\rho = 0.6$ which corresponds to a clear weather, but also for $\rho = 0.06$ which corresponds to a

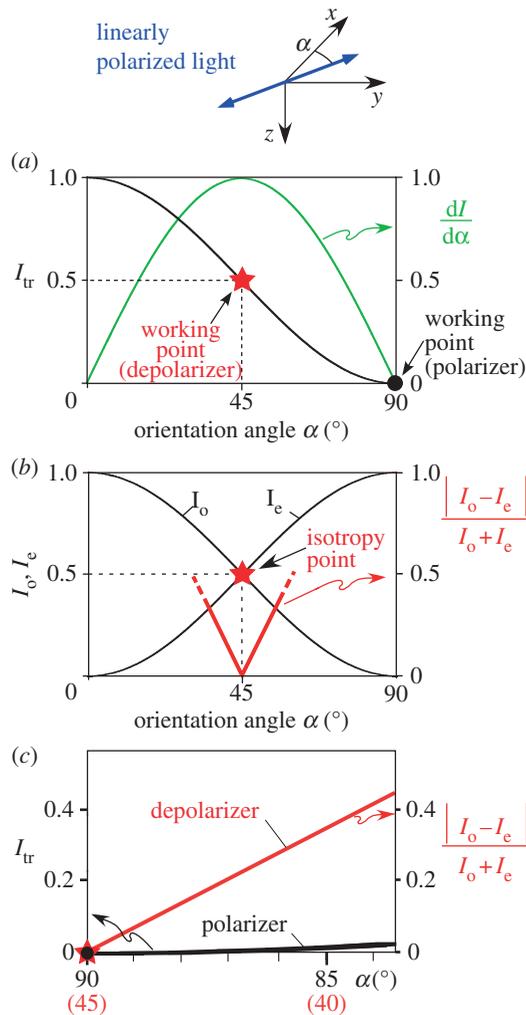


Figure 3. Case of a linearly polarized light. Comparative methods for the use of the Malus' law for the two working points corresponding to a polarizer and a depolarizer. (a) The Malus' law with its two possible working points and its derivative. (b) Theoretical contrast on both sides of the 45° isotropy point of the calcite. (c) Comparative signal intensities for the polarizer and the depolarizer methods around their respective working points. (Online version in colour.)

rather foggy sky, the signals are clearly above the eye contrast threshold. To test the Alderney-like crystal, we have first to record the typical intensity profiles of the light of the sky at the zenith, and second to investigate its potential via differential observations around the 45° working point, avoiding stray lights using an opaque protection.

3. Results

(a) Spectroscopical analyses: ion exchange results

As shown in figure 5a, the ICP-AES technique appears well suited for bulk analysis and namely for detecting calcium, the main element in the CaCO_3 crystals. The comparison of the atomic emission signature for the Alderney crystal and for a reference freshly collected calcite crystal is performed at around 317.9 nm (figure 5a). The two spectra are quite similar, confirming chemically the calcite nature of the Alderney crystal.

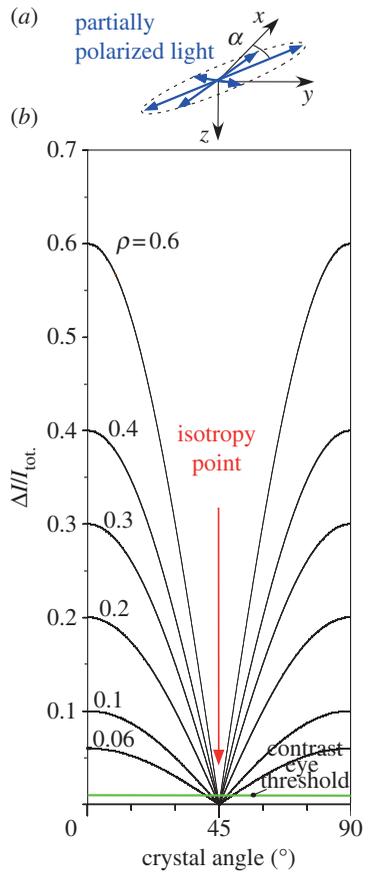


Figure 4. (a) Case of a partially polarized light. (b) Theoretical V-shaped contrast signals for different degrees of polarization encountered in the English Channel. The horizontal line represents the contrast eye threshold introduced by Hubel [22]. (Online version in colour.)

The relative measured concentration of Mg^{2+} traces (using the same ICP-AES technique) in the Alderney crystal compared with a freshly collected calcite is shown in figure 5b. The Mg^{2+} concentration in the Alderney crystal has been increased by a factor eight, as shown by the emission spectra around 279.5 nm, reaching 2000 ppm. As the Ca^{2+} ion has a larger diameter (0.1 nm) than the Mg^{2+} ion (0.07 nm) the crystalline structure of the calcite at the surface is known to be slightly compressed, then reducing the transparency, but increasing the insolubility and strengthening the crystal [23,24]. This explains the good conservation of the rhombohedral geometry of the Alderney crystal, keeping the typical 102° and 78° angles even after a long stay in sea water. Note that active sites such as dislocations, micro-fractures and point defects increase the ion exchange rates reaching the bulk of the crystal.

The surface analysis brings additional information to the bulk analysis, namely for the crystal transparency. We have carried out several tests on cleaved calcite crystals partially immersed in $MgNO_3$ solutions in water. After only a few days, the typical Ca–Mg ion exchanges are already directly observable with the naked eye as shown in the photograph of figure 6. Scanning electron microscope measurements allow discrimination between the non-immersed cleaved calcite region and the immersed calcite region. The corresponding energy-dispersive X-ray spectra are shown in figure 6a for the pure $CaCO_3$ calcite and in figure 6b, for the Mg–Ca calcite after only a two-week immersion. Now, if we immerse the crystal directly in sea water taken from the English Channel, the change in the transparency remains observable with the naked eye as shown in the photograph of figure 7. The spectrum of the non-immersed surface shown in

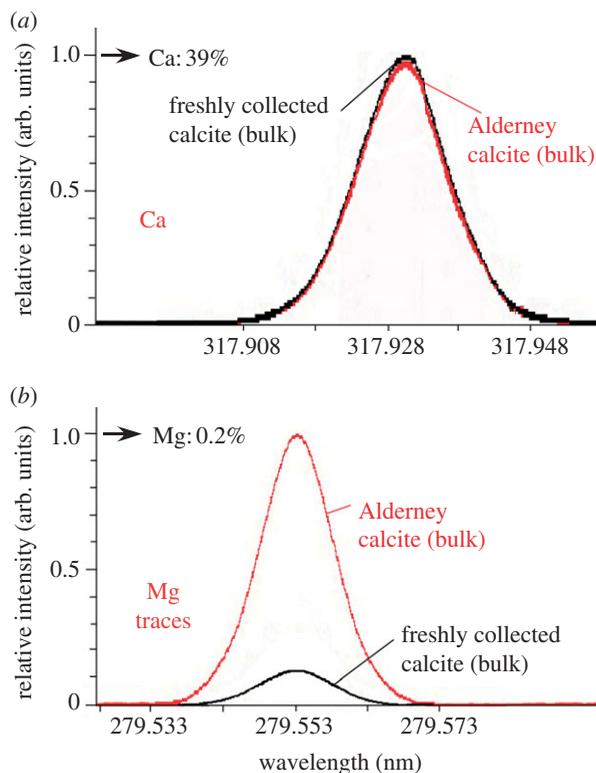


Figure 5. Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) spectra for the bulk of a freshly collected calcite crystal and of the Alderney crystal. (a) Both crystals exhibit the same 317.9 nm calcium peak, confirming that the Alderney crystal is a calcite crystal. (b) Comparison of Mg traces in both crystals at 279.5 nm. The Alderney crystal exhibits an Mg concentration eight times greater than that for a freshly collected calcite. (Online version in colour.)

figure 7a is similar to the one shown in figure 6a, but the spectrum of the figure 7b shows a 0.27 per cent concentration of Mg and an additional contribution of sodium and chloride ions, the NaCl salt being clearly apparent on the electron microscopy photograph. These relatively rapid surface effects, although reducing the crystal transparency, constitute a thin protecting envelope around the calcite crystal and contribute to its good conservation as in the case of the Alderney crystal.

(b) Sand abrasion

Moreover, when excavated, the Alderney crystal was covered with sand. So another contribution to the semi-opacity of the crystal results from its surface roughness associated with the unavoidable sand abrasion in the very strong tidal sea water currents that run around Alderney. On the Mohs scale, silica sand usually in the form of quartz, has a hardness of 7. After sand abrasion and an additional two-week immersion in sea water, the crystal of figure 1b looks like the semi-opaque crystal of figure 1c with a white rough surface. The measured roughness of the crystal before and after the abrasion by sand is shown in figure 8a, b, respectively. While the roughness of the crystal is initially undetectable (figure 8a), the mean roughness of the surface in figure 8b is about $1.2\ \mu\text{m}$, i.e. a value larger than the wavelength of the visible light. Mie scattering [20] is then the major scattering for white light impinging on the crystal. Mie scattering does not depend on the wavelength, so the crystal appears white. Moreover, the sand abrasion increases drastically the contact surface between the crystal and the sea water, reinforcing the ion exchanges. Taking into account both ion exchanges and sand abrasion, the initial transparency of the crystal is largely reduced, but its typical rhombohedral geometry is well preserved.

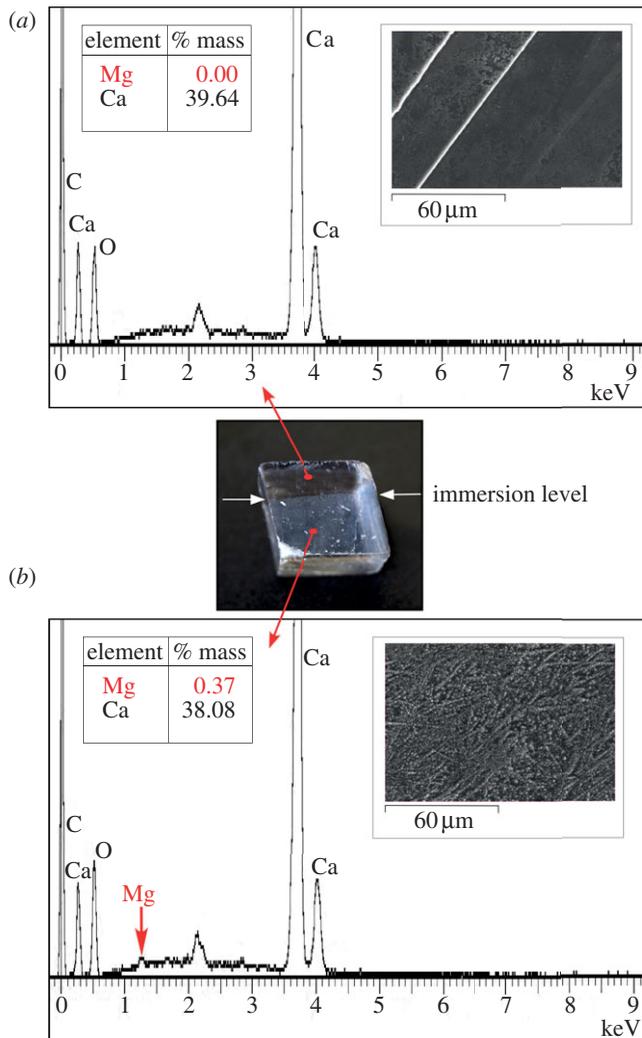


Figure 6. Mg^{2+} – Ca^{2+} exchanges on calcite surface for a crystal partially immersed in a solution of MgNO_3 in water. The photograph shows the two parts of the crystal after a two-week immersion. The upper part has remained transparent while the lower part shows a reduction of the transparency which can be observed directly with the naked eye. (a) For the non-immersed part, no Mg^{2+} ion is detected in the measured energy-dispersive X-ray spectrum. The electron microscopy photo of the surface, in the inset, shows the unchanged quality of the surface. (b) For the immersed part, the expected Mg signature appears at 1.3 keV, corresponding to a measured 0.37% concentration. The electron microscopy photo of the corresponding surface, in the inset, confirms the reduced transparency of the surface. (Online version in colour.)

(c) Magnetic tests

Before taking optical bearings with an Alderney-like crystal, when the Sun is hidden, let us examine some of the navigation problems linked to the use of magnetic compasses, particularly before 1600. The magnetic needle introduced in Europe, in the thirteenth century, rapidly played a crucial role in navigation. However, one has to wait for Gilbert to understand the main basic points in magnetism [16]. Gilbert's greatest contribution in magnetism was his conception of the Earth itself as a great magnet [17]. He was also aware of the local anomalies of the Earth's magnetic field and of the deviations of the compass needle near ferromagnetic objects, trying to discard many stories [17] concerning supposed or real magnetic effects. Let us measure the

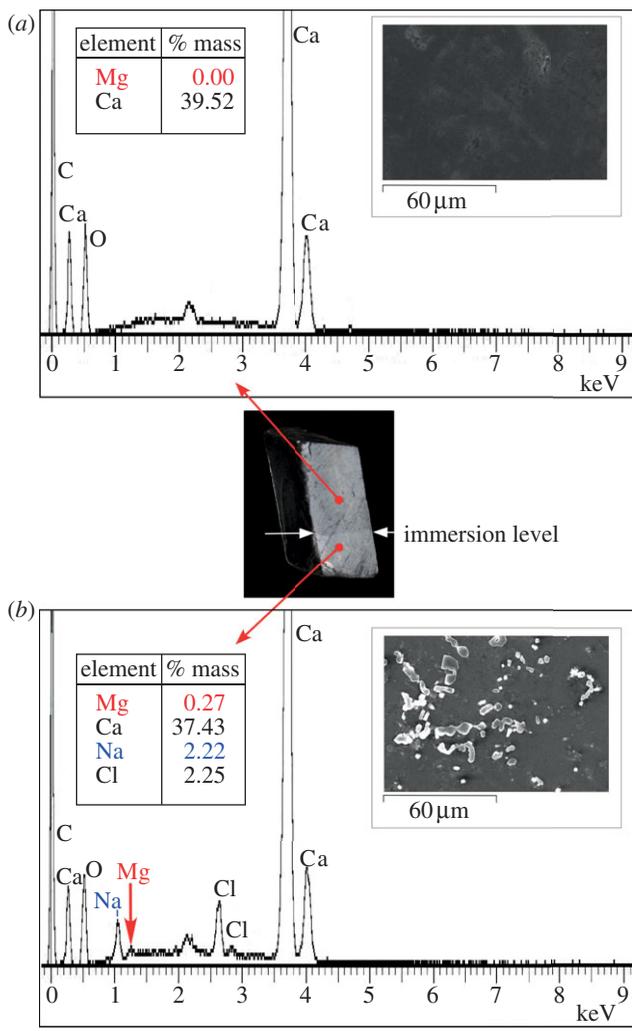


Figure 7. Mg^{2+} – Ca^{2+} exchanges on calcite surface for a crystal partially immersed in sea water. The photograph shows the two parts of the crystal after a two-week immersion. The upper part has remained transparent while the lower part shows a slight reduction of the transparency which can also be observed directly with the naked eye. (a) For the non-immersed part, no Mg^{2+} ion is detected in the energy-dispersive X-ray spectrum. The Electron Microscopy photo of the surface, in the inset, shows again the unchanged quality of the transparent surface. (b) For the immersed part, the expected Mg signature also appears at 1.3 keV, corresponding to a measured 0.27% concentration. Note that in sea water an additional Na peak appears at 1.05 keV on the spectrum. The NaCl deposition on the crystal surface is clearly observed on the Electron Microscopy photo in the inset. (Online version in colour.)

possible variations that a magnetic compass could undergo on board a ship in the Elizabethan age. Indeed, the Alderney ship was full of metallic weapons, including cannons, helmets, body armours, muskets, etc. When a magnetic compass is located near one of the excavated cannons of the Alderney shipwreck, the observed deviations are reported in figure 9. We can see that the perturbations reach about 100° . Although at the end of the sixteenth century, Gilbert was able to explain the basic properties of the magnetic compass, many phenomena remained mysterious like the magnetic shielding and the deviations from the true North. So, an optical compass could be a plausible tool for trying to correct magnetic errors. In particular, at twilight when the Sun is no longer observable being below the horizon, and the stars still not observable, this optical device could provide the mariners with an absolute reference in such a situation.

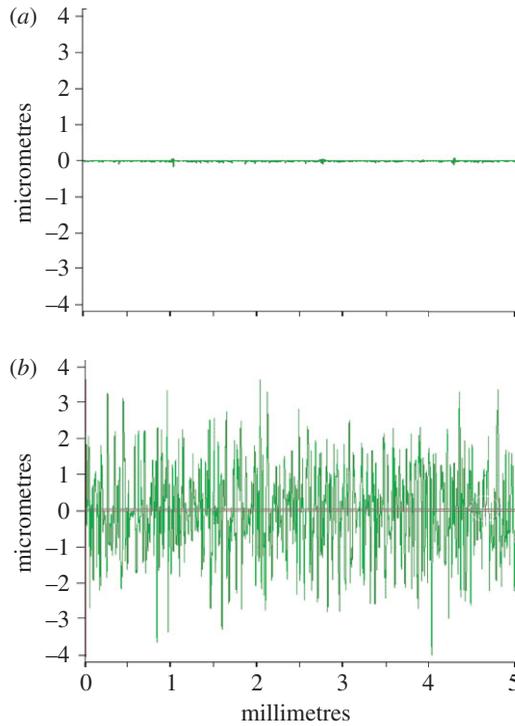


Figure 8. Comparative roughness measurements obtained with a Taylor-Hobson surface profiler. (a) For the transparent crystal of figure 1*b*. (b) For the same crystal after sand abrasion and a two-week immersion in sea water (see the corresponding photograph in figure 1*c*). The mean roughness reaches 1.2 μm , resulting in strong Mie scattering of the visible light. (Online version in colour.)

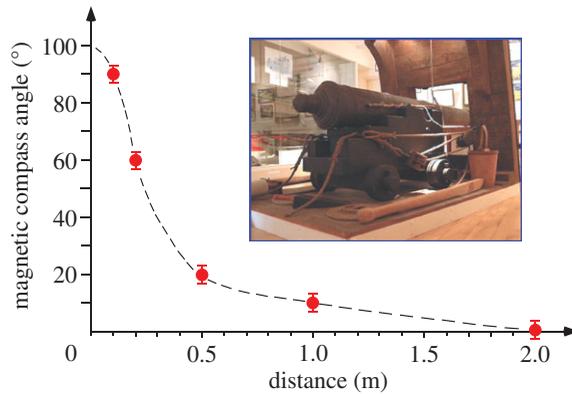


Figure 9. Typical perturbations of a magnetic compass by one of the excavated cannon of the Alderney ship. The dashed line is only a guide to the eye. The weight of the cannon is 700 kg. The axis of the cannon is oriented about the east–west direction. The magnetic compass is moved perpendicularly to the axis of the cannon. In this case, the deviations can reach 100°. The inset shows a photograph of the cannon exhibited at the Alderney Museum. (Online version in colour.)

(d) Optical results with an Alderney-like crystal

Let us first record the low sky luminosity at twilight, in clear weather, when the Sun disappears below the horizon. The successive photographs in figure 10*a* were taken with a 10-min interval on 18 April 2011, at the latitude of 48°07' N and at the longitude of 1°41' W. Measuring the

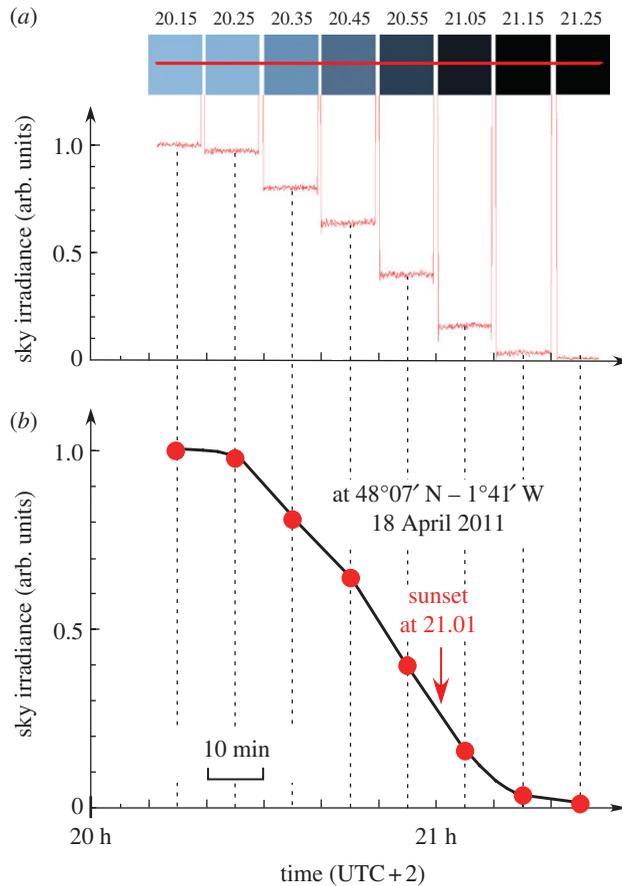


Figure 10. Typical measured sky irradiances at twilight on 18 April 2011 at $48^{\circ}07' \text{ N}$, $1^{\circ}41' \text{ W}$. (a) The successive photographs are taken within 10 min intervals. A densitometer allows us to measure the irradiances. (b) Corresponding experimental variations versus time. Note that the first stars became observable at about 21.00 (local summer time = UTC + 2, UTC: Universal Time Code). (Online version in colour.)

successive irradiance densities, we obtain the typical luminosity decay as shown in figure 10*b*. At 21.15, for instance, the sky irradiance is already reduced by a factor 20 compared with the irradiance 1-h before, at 20.15. Using an Alderney-like crystal, we tried to determine the direction of the hidden Sun in similar conditions on 28 July 2011 as shown in figure 11. The corresponding celestial irradiances are shown in figure 11*a* before, and just after the emergence of the first stars. Typical observations through the Iceland spar are shown in figure 11*b*. The differential irradiances for different orientations of the Iceland spar are reported in figure 11*c*. The experimental measurements are in good agreement with the theoretical curve corresponding to the polarization degree $\rho = 0.6$ measured on that day. Even with these low luminosities, we note that the Sun direction can be determined using an Alderney-like crystal with great precision, in the degree range.

Moreover, one may wonder if the high sensitivity of the human eye could allow the sailors to use such calcite crystals as Sun followers, when the Sun is completely below the horizon, as shown in figure 12*a*. We took the Sun bearing every 10 min from 19.00 to 20.30 on 30 September 2011. The corresponding experimental observations are reported on figure 12*b*, with the predicted theoretical solar azimuth calculated for $48^{\circ}07' \text{ N}$ latitude, taking into account the Earth's rotation. These results show that the Iceland spar behaves as a powerful differential tool, for the location of a hidden Sun and could provide the navigators with an absolute reference particularly in dark situations around sunset or sunrise.

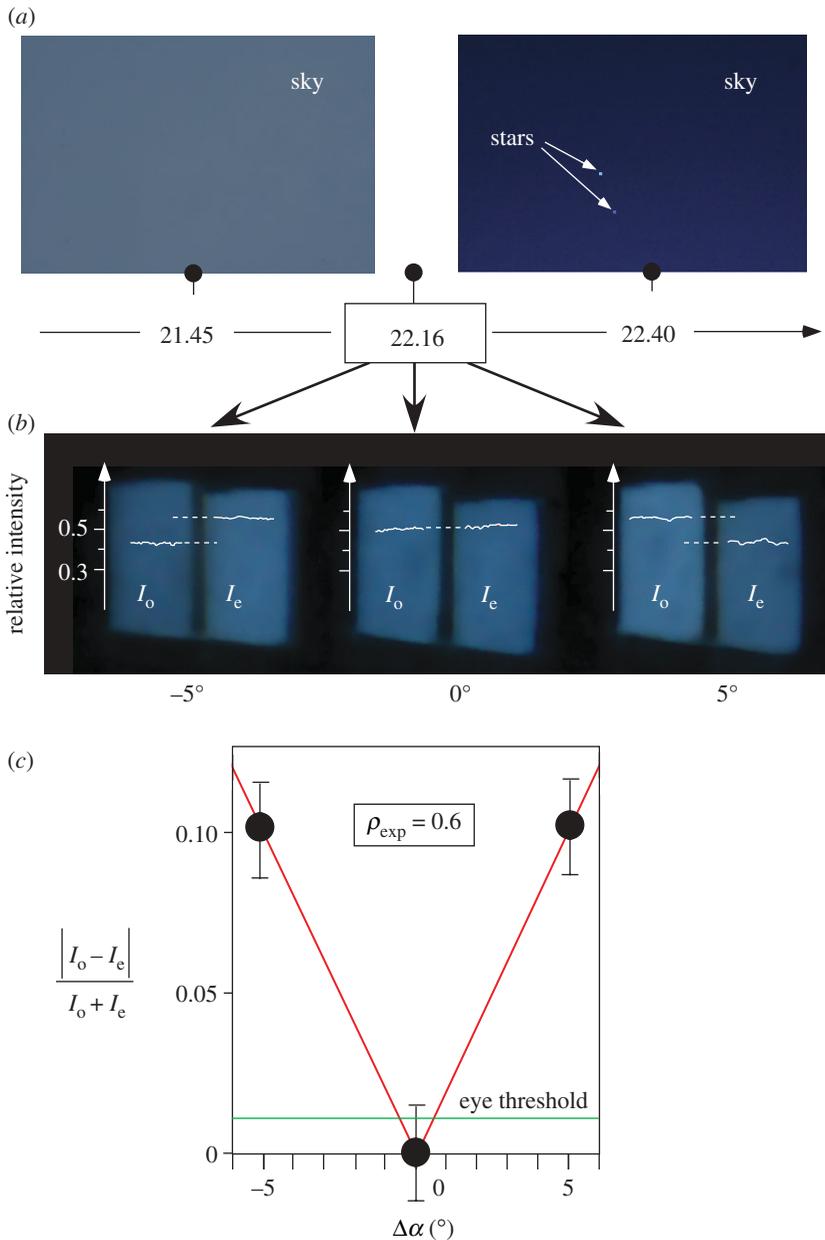


Figure 11. Typical bearing of the Sun at 22.16 during twilight for low irradiances. (a) Celestial irradiances before and after the emergence of the first stars on 28 July 2011. (b) Experiment performed a quarter of an hour before the stars appear. The white lines correspond to the relative intensities of the ordinary and extraordinary beams. The degree of polarization is $\rho = 0.6$. (c) The contrast remains clearly above the contrast eye threshold of 1%. The precision of the Sun bearing is in the degree range. (Online version in colour.)

4. Discussion and conclusions

The Alderney Elizabethan shipwreck is the first ancient shipwreck with a calcite crystal found on board. The main chemical activity of sea water and the mechanical sand abrasion during the four-century immersion, explain both the good geometrical conservation of the crystal, but also the reduction of its optical transparency. One of us (S.W.) who discovered the crystal, notes that his

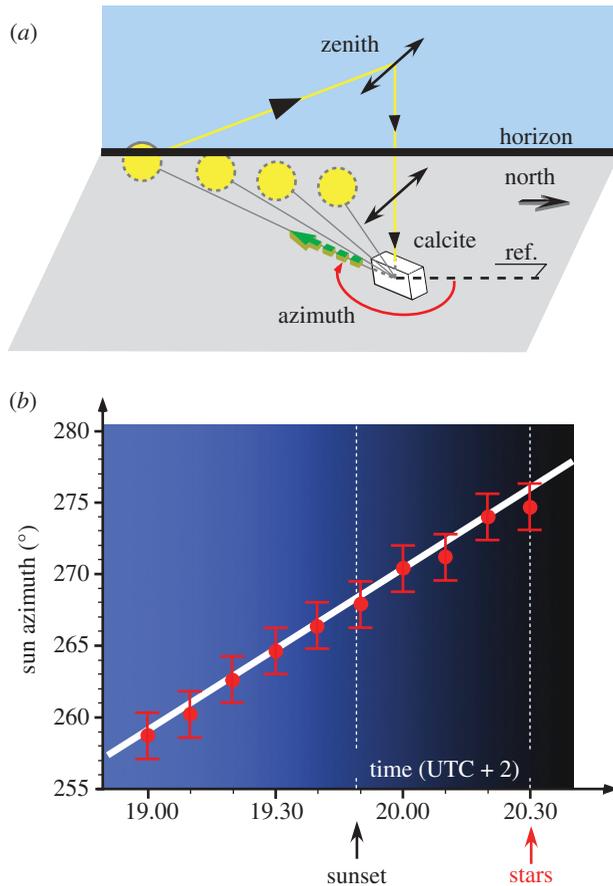


Figure 12. Sun tracking experiment (see panel *a*). On 30 September 2011, we reported the successive experimental bearings versus the time between 19.00 and 20.30 (*b*). Each experimental point (dot) has been measured five times. The straight line corresponds to the theoretical azimuths of the Sun at $48^{\circ}07' \text{ N}$, $1^{\circ}41' \text{ W}$, taken from the National Geographical Data Center. Due to the precision of the Sun bearing the sailors were able to follow the Sun below the horizon. (Online version in colour.)

attention was only drawn to the regular rhombohedral geometry of the stone. Moreover, a pair of navigation dividers was also found in the same location and it may indicate that it was kept with other navigational tools. Although easy to use, the magnetic compass was not always reliable in the sixteenth century, as most of the magnetic phenomena were not understood. If the time was correctly known from the navigator's internal clock [25,26] and hourglasses, the calcite sunstone would make it possible to check and recalibrate the magnetic information. Note that, as pointed out by Pye [3] and by Horváth & Varjú [27], it has been suggested that migrating birds may use sky polarization as an aid to navigation. Indeed for migratory songbirds, the multiple compass systems have also to be recalibrated [28] when exposed to conflicting directional information, for example, when magnetic declination changes specially at high latitudes. Muheim *et al.* [28] have shown that the migratory Savannah sparrows use polarized light cues to recalibrate their magnetic compass around both sunrise and sunset. In the same manner, as the magnetic compass on a ship can be perturbed for various reasons, the optical compass giving an absolute reference, may be used when the Sun is hidden.

Curiously, in the recent successful detection of the very weak beams of polarized light scattered from the atmosphere of an Earth-like exoplanet (HD189733b), the authors [29] use the same calcite method (but with the screen being located after the crystal), furthermore eliminating the stray polarization effects owing to the Earth's atmosphere.

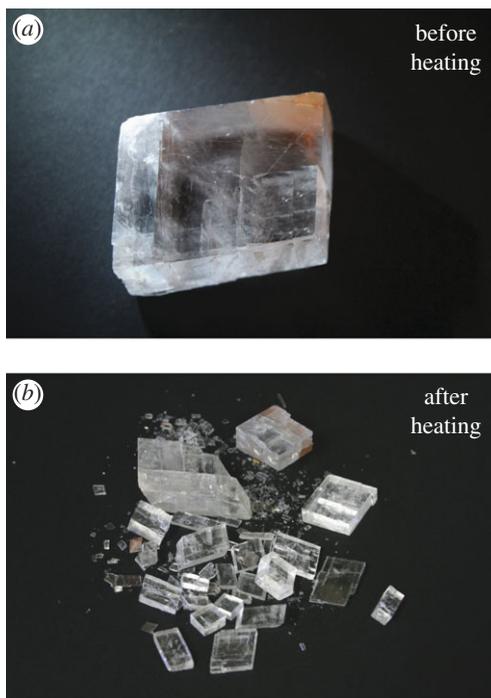


Figure 13. Heating of a calcite crystal. (a) Photo of a $5 \times 3.5 \times 1.5$ cm crystal before heating. (b) Photo of the calcite fragments after heating at 250°C for 10 min. Note that the fragments have kept a rhombohedral geometry. (Online version in colour.)

Although the calcite is rather fragile, the Alderney crystal brings new insights for the search of similar crystals. In shipwrecks, when the calcite has been immersed for centuries in sea water, the crystal transparency is lost mainly because of the Mie scattering and the ion exchange strains, but the typical rhombohedral geometry is nicely preserved. Moreover, one may note that calcite has the tendency to fracture along structural planes. The planes of cleavage of comparative weakness, as a result of the regular arrangement of atoms in the crystal can break the calcite crystal, especially when heated. Figure 13a shows a typical calcite crystal, which breaks when heated only at 250°C for about 10 min, resulting in small rhombohedrons (figure 13b). Viking practice of cremation probably reduces the possibility for archaeologists to find complete crystals among the artefacts in the Viking burials explored in different locations. However, as in figure 13b, the fragments keep their typical 102° and 78° angles.

Moreover, it is worthwhile noting that although the history of the Iceland spar before Bartholin's discovery in 1669 is not well known, the calcite quarries already existed in Iceland in the fifteenth and sixteenth centuries [8], perhaps since the time of the Vikings. Indeed in a recent excavation in Iceland, a first calcite fragment was discovered in a Viking settlement [30], proving that some people in the Viking age were employing Iceland spar crystals (Á. Einarsson 2012, private communication). The Alderney discovery and these recent findings lend hope for discovering other crystals or fragments in the different archaeological Viking sites or ancient shipwrecks, similar to those explored in Scotland, Ireland, Iceland, Greenland and Scandinavia.

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