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The inventory of water and carbon dioxide reservoirs on Mars are important clues for understanding the geological, climatic and potentially exobiological evolution of the planet[1]. From the early mapping observation of the permanent ice caps on the martian poles[2,3], the northern cap was believed to be mainly composed of water ice, whereas the southern cap was thought to be constituted of carbon dioxide ice. However, recent missions (NASA missions Mars Global Surveyor and Odyssey) have revealed surface structures[4], altimetry profiles[5], underlying buried hydrogen[6], and temperatures of the south polar regions that are thermodynamically consistent with a mixture of surface water ice and carbon dioxide[7]. Here we present the first direct identification and mapping of both carbon dioxide and water ice in the martian high southern latitudes, at a resolution of 2 km, during the local summer, when the extent of the polar ice is at its minimum. We observe that this south polar cap contains perennial water ice in extended areas: as a small admixture to carbon dioxide in the bright regions; associated with dust, without carbon dioxide, at the edges of this bright cap; and, unexpectedly, in large areas tens of kilometres away from the bright cap.

The ESA/Mars Express Orbiter[8] was inserted into Mars orbit on 25 December 2003. The Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) instrument[9], one of the seven investigating instruments on board, is an imaging spectrometer analysing the diffused solar light and the planetary thermal emission. On each resolved pixel, 1.2 mrad in the instantaneous field of view, OMEGA acquires a spectrum in 352 contiguous spectral channels from 0.35 to 5.1 μm, with a spectral sampling ranging from 7 nm (in the visible) to 13 nm (from 1.0 to 2.7 μm) and 20 nm (from 2.7 to 5.1 μm). A few initial observations were performed soon after Mars orbit insertion, in particular while the spacecraft was overflying the south polar areas. The altitude of observation ranged from ~1,500 km to ~2,000 km, providing an OMEGA surface sampling of ~2 km. OMEGA thus mapped a large fraction of the south polar regions, along four distinct orbits, from 18 January to 11 February 2004 (solar longitude, $L_{\odot} = 335°$ to 348°)—that is, about one month before the martian southern autumn equinox. At the time of the observations, the Sun's elevation was very low (<10°); however, given the very high performances of OMEGA, several tens of thousands of spectra were acquired with signal-to-noise ratios of >100 over almost the entire spectral domain. From the acquired spectra, it is possible to derive coupled maps of a variety of parameters and properties: in particular, the major icy constituents, CO_2 and H_2O, have several unambiguous diagnostic spectral signatures enabling the mapping of their respective distributions over the imaged areas (see below).

The OMEGA spectral images exhibit well-characterized high albedo perennial polar ice patterns. From their near-infrared spectrum, we can assert that these bright areas are those where

CO_2 ice is highly concentrated (Fig. 1a).

A crucial finding is the identification of H_2O ice, with a varying concentration over a much larger area (Fig. 1b). H_2O ice is found in three distinct units, as follows.

Unit 1. On the bright cap. In this unit, water ice is mixed with large concentrations of CO_2 ice. This makes its spectral identification more difficult than in the two other units, as CO_2 ice exhibits spectral features in the same spectral domain. It requires a careful analysis, illustrated in Fig. 2, where a typical OMEGA spectrum of a pixel located in this CO_2 ice cap is compared to modelled spectra obtained with either pure CO_2 ice or a mixture of H_2O ice and CO_2 ice. We show that pure CO_2 ice cannot account for the observed spectra: the presence of H_2O ice is required. The best fit is obtained with a mixture of 15 wt% H_2O ice, in the form of an intimate molecular mixture, rather than a simple geometrical mixture of two pure components.

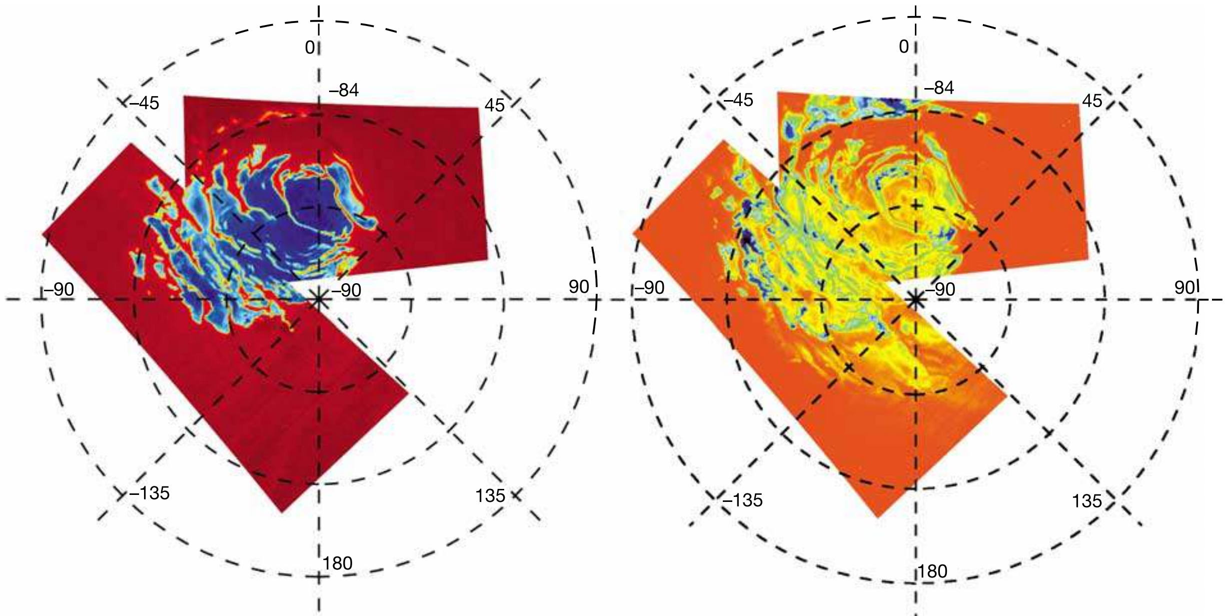

Figure 1 Global maps of CO_2 and H_2O ices at the south pole of Mars. Left, the CO_2-ice absorption feature is scaled from blue (deep) to brown (CO_2-ice-free areas); right, mapping of the H_2O ice, from blue (deep absorption) to red (ice-free). Comparison shows that the H_2O-ice areas extend far beyond the CO_2-rich bright cap, along its scarps up to isolated units tens of kilometres wide.

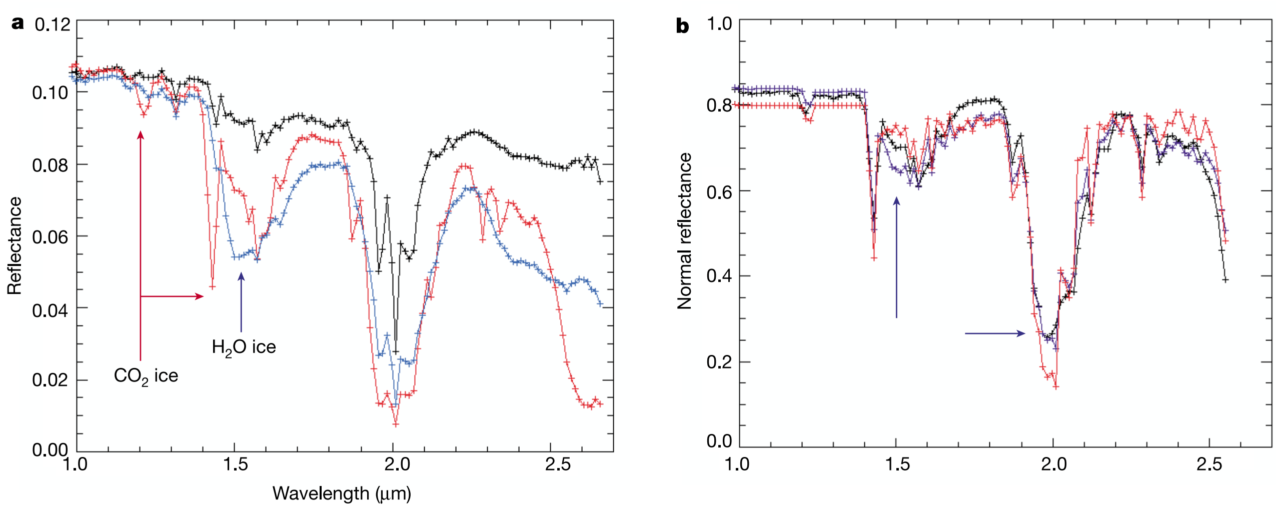

Figure 2 Near-infrared spectra of CO_2 ice and H_2O ice in Mars polar units. **a**, 1.0 to 2.6 μm part of spectra acquired by OMEGA on an ice-free zone (black), on the CO_2-ice-rich bright cap (red) and on an H_2O-ice-rich scarp (blue). In addition to the major atmospheric spectral features, they exhibit the specific CO_2 and H_2O ice absorptions, some of them being indicated (arrows). The scarps are seen to have none of the numerous CO_2-ice diagnostic features. **b**, OMEGA spectrum of a pixel located on the CO_2-rich cap (black), after removal of the atmospheric contribution, is compared to the best-fit modelled spectrum of a sample containing CO_2 ice only (red, r.m.s. = 0.057) and to the spectrum of a mixture of CO_2 and H_2O (blue, r.m.s. = 0.035), indicating that some H_2O is required to account for the pattern observed at 1.5 and 2.0 μm (arrows). The H_2O/CO_2 ratio providing the best fit is 15 wt% H_2O, in the form of an intimate mixing. However, some departure from the actual spectrum is still present, mainly at 1.5 μm; this could be accounted for by a complex mixture including H_2O/CO_2 clathrate, which could not yet be simulated in the absence of relevant optical constants. The synthetic spectra have been calculated using the Shkuratov–Poulet[15] model.

Unit 2. On the scarps around the residual cap. This H_2O ice is almost completely CO_2-ice-free, and appears darker than the surrounding bright CO_2-ice-rich cap; Fig. 3 illustrates the correlation between the albedo, the H_2O content and the CO_2 content of the ice: the darker the ice, the richer it is in H_2O, and the more depleted it is in CO_2.

Unit 3. Along vast zones expanding down slope in stratified terrains, tens of kilometres wide, and tens of kilometres away from the CO_2-ice-rich perennial caps. These water-ice-rich areas are CO_2-free: they appear much darker than the bright CO_2-ice-rich cap, both in the visible and the near-infrared, which reflects their high dust concentration, and would confirm the scenarios where H_2O precipitates together with dust. The OMEGA processed data show that the H_2O-to-dust ratio varies, with no clear correlation with the local topography or relief (Sun illumination angle).

The OMEGA units 2 and 3 partly match the Af unit in the USGS I-2686 geological map[10]. Af is defined on the basis of its albedo and colour, found to be "intermediate between those of residual polar ice cap and dust unit"[10]. The Af unit is interpreted as a "mixture of CO_2 frost and defrosted ground"[10], while the OMEGA observation shows CO_2-ice-free exposed mixtures of water ice and dust.

Figure 4 illustrates the relation found between the composition as inferred from the OMEGA spectral images and the surface morphology revealed by the Mars Orbiting Camera (MOC) high-resolution images on the Mars Global Surveyor (MGS) mission. From right to left of the MOC strip (Fig. 4d), we observe the bright polar ice, which exhibits irregular patterns similar to 'Swiss cheese' (ref. 11); OMEGA results demonstrate that this area is predominantly constituted of CO_2 ice. It is followed by the H_2O-ice-rich areas, free of CO_2, which by contrast are characterized by very smooth surfaces. Within these H_2O-ice-rich areas, close to the CO_2 ice, we observe polygonal features; this structure is consistent with

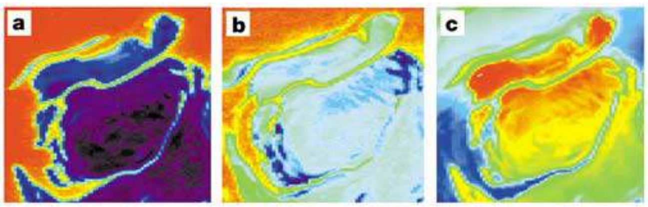

Figure 3 Correlated variations of the CO_2 ice, H_2O ice and albedo. **a**, Map of the CO_2 ice, from deep blue (higher concentration) to red (ice-free), matching the bright cap, centred around 87° (latitude) and 0° (longitude). **b**, Same area mapped for its H_2O-ice content. **c**, Same area, seen in its near infrared *I*/*F* (intensity divided by solar flux), from dark (blue to green) to bright (red). Local *I*/*F* variations within the cap are clearly correlated to the H_2O/CO_2 ratio: the bluest water-ice areas are highly depleted in CO_2, and darker, while the brighter areas are those where H_2O is depleted in favour of CO_2.

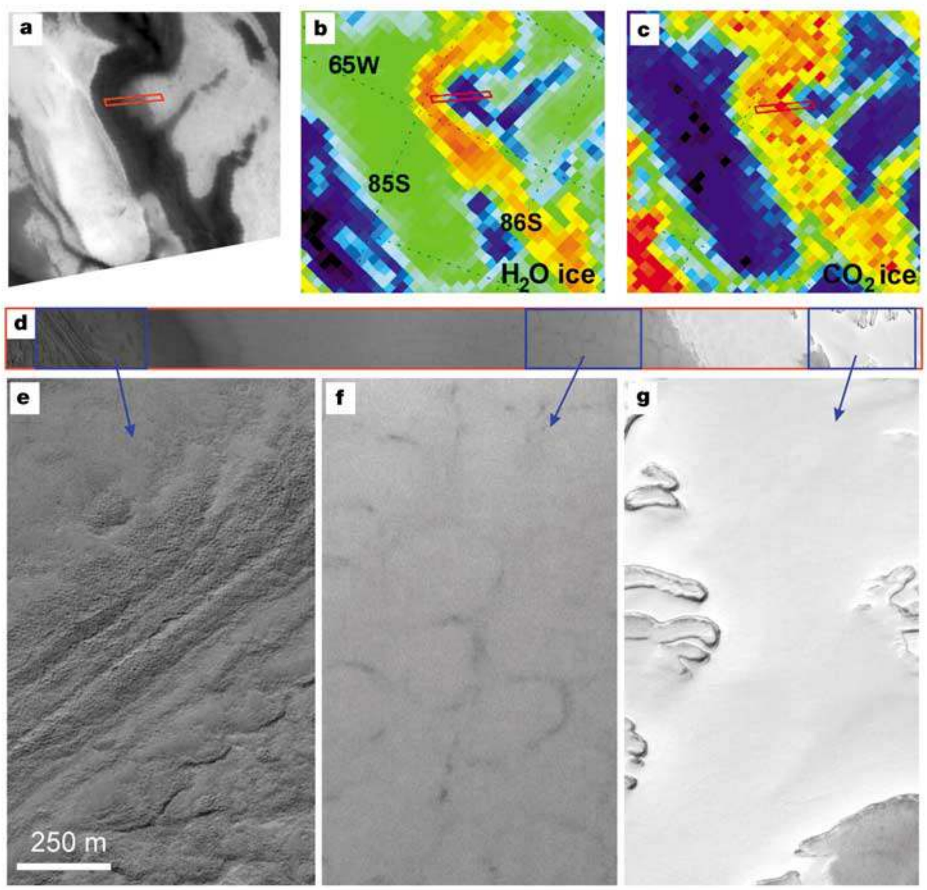

Figure 4 Transition from CO_2 ice to H_2O ice. **a**, MOC (NASA/JPL/MSSS) context image, exhibiting the bright polar areas. **b**, Map, within the same area, of the H_2O ice as identified by OMEGA (processed 1.5 μm feature, see Fig. 2), with a blue to red colour scale; the bluest is the richest in H_2O. **c**, Same mapping of the CO_2-ice features. **d**, Enlargement of the strip (image M13-01891, at $L_\odot = 325.3°$) marked by the red rectangles in **a**, **b** and **c**. It exhibits the variety of terrains identified by the MOC, examples being enlarged following the arrows (**e**, **f**, **g**), from the bright 'Swiss cheese'-like structured ice, towards the dark layer terrain on the left. The OMEGA-derived maps indicate the composition of each unit: CO_2-rich ice for the bright unit; ice-free for the layer terrains; and H_2O ice for the smooth dark terrains in between, with polygonal structures closer to the bright cap. These structures can also be observed in the transition zone (between **f** and **g**), through a thin covering layer of CO_2 ice.

them resulting from thermal retraction. At the transition between the bright cap and the smooth dusty (darker) H_2O-ice-exposed units, these polygonal features are seen through a thin and bright CO_2 ice layer. The ice-free stratified terrains expand then to the left of the image.

Wherever CO_2 ice is stable, it traps solid H_2O. OMEGA data show large areas where CO_2 ice has sublimated away, while water ice remains, mostly mixed with dust. The perennial southern cap thus by far exceeds the bright CO_2-rich icy area. Moreover, the lack of slope change at the transition between the bright cap and the surrounding water-ice polygonal areas is an indication that the CO_2-ice layer might well be restricted to a fairly thin layer, no more than some metres in depth, in agreement with previous estimates derived from shadow measurements in quasi-circular depressions[11]. OMEGA spectral images of the bright cap and of its scarps are consistent with a model in which H_2O ice is present in the underlying material, a scenario which has been proposed to explain the morphology of the 'Swiss cheese' terrains[12].

The underlying material, over 1–3 km in thickness and some 400 km in size, according to the Mars Orbiter Laser Altimeter (MOLA) polar cap profile, is likely to constitute a distinct geological unit as inferred from its morphology[11]. The direct OMEGA surface compositional measurements support a model in which the bulk of this unit is constituted of dust mixed with water ice, as predicted by mechanical modelling[13]. The perennial south polar cap would then constitute a significant fraction of the overall H_2O reservoir. Conversely, if CO_2 ice is indeed restricted to the bright areas, possibly concentrated in a thin surface veneer, it would not constitute a major sink for the initial atmospheric CO_2.

The inventory of condensed volatiles on Mars, in all potential phases (gas, clouds, hydrated minerals, frosts, ices, permafrost, liquids), at and below its surface, is central to understanding the evolution of the planet, from geological timescales to seasonal variations. Part of the answer to the question of Mars having harboured life in the past, and to the issue of Mars hosting future human exploration, is to be deciphered in this inventory. This is why contributing to this inventory, in particular on the poles, remains a major goal for Mars space exploration[14]. With the ongoing Mars Express mission just starting its global coverage of Mars, OMEGA will continue mapping the CO_2 and H_2O condensation/sublimation cycles at all south and north latitudes; the goal is to provide a quantitative evaluation of the seasonal and perennial condensed reservoirs of these crucial volatile species. In parallel, the Mars Advanced Radar for Subsurface and Ionosphere Sounding (MARSIS) experiment will start its mapping phase in May 2004. It should enable an accurate determination of the volume of the H_2O-ice-rich surface permafrost identified by OMEGA at the south pole, and compare it with a potential subsurface permafrost considered up until now to be the major Mars water reservoir.

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