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The Phase Composition of Triton's Polar Caps

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Triton's polar caps are modeled as permanent nitrogen deposits hundreds of meters thick. Complex temperature variations on Triton's surface induce reversible transitions between the cubic and hexagonal phases of solid nitrogen, often with two coexisting propagating transition fronts. Subsurface temperature distributions are calculated using a two-dimensional thermal model with phase changes. The phase changes fracture the upper nitrogen layer, increasing its reflectivity and thus offering an explanation for the surprisingly high southern polar cap albedo (approximately 0.8) seen during the Voyager 2 flyby. The model has other implications for the phase transition phenomena on Triton, such as a plausible mechanism for the origin of geyser-like plume vent areas and a mechanism of energy transport toward them.

Since the discovery of N_2 on Triton (1), Neptune's largest moon, and especially since the Voyager flyby (2), there have been several attempts to model the transport of volatiles on Triton in response to its complex seasonal cycle (3). It has usually been assumed that the albedo distribution on Triton is the result of the seasonal N_2 transport (4–8), but so far no models have successfully reproduced the observed albedo pattern.

An understanding of the mechanisms driving the albedo distribution is somewhat incidental to the question of the vertical phase composition of N_2 ice deposits on Triton. Ground-based spectral measurements show that Triton's illuminated surface is mostly covered with frozen N2 at least many centimeters deep (1). The mean insolation on Triton is greatest at the equator and smallest at the poles (4, 5, 9). As a result, any N2 in excess of that which can be sublimated and recondensed during one of Triton's extreme seasons (3) is transported to permanent polar caps, which may be several hundred meters thick and extend as far toward the equator as $\pm 45^{\circ}$ of latitude, depending on Triton's total inventory of surface N_2 (8). The seasonal redistribution of volatiles also causes global temperature variations on time scales of a few tens of years (4, 5, 10), which can be as much as 15 to 20 K or as little as 2 to 4 K, depending again upon the total surface inventory of N_2 . Furthermore, the 38 K temperature of Triton's lower atmosphere is thought to be representative of all the N₂ ice on Triton's surface (4, 5) and is perilously close to the temperature (35.61 K) of the α - β (cubichexagonal) phase transition in solid N₂.

The subsurface ice layer on Triton is therefore likely to experience the passage of multiple phase transition fronts as the global temperature oscillates above and below 35.61 K. Besides the absorption and liberation of latent heat at the phase transition, there is also a large change in volume over a small range in temperature: Laboratory measurements indicate that the density of solid N_2 changes by 1 to 2% in a range of about 1 K around 35.61 K (11). The induced stresses cause severe fracturing of the crystalline solid when the transition is from the β to the α phase (11). (To our knowledge, experiments to determine whether α -N₂ crystals shatter when the phase transition is approached from lower temperatures have not been done; experiments (11) have dealt only with powdered α -N₂ because large crystals are difficult to obtain.)

We assume that Triton is completely differentiated (2, 8), with a silicate core of radius ~1000 km overlain by a water-ice mantle about 350 km thick and a thin veneer of solid N_2 , no more than 1 km thick. We include in our heat transfer model the effect of the reversible phase transition from the denser cubic α phase to the hexagonal β phase that occurs when the temperature rises to 35.61 K (for the ¹⁴N₂ isotope at equilibrium vapor pressure), at which latent heat of 55.62 cal/mol for the ¹⁴N₂ isotope (11) is absorbed. The

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phase transition is driven primarily by seasonal variations in a globally uniform surface temperature, caused mostly by changes in N_2 coverage on Triton's illuminated hemisphere that occur when N_2 sublimates and recondenses in response to seasonal changes in the distribution of absorbed insolation (4–8).

The global temperature changes are also coupled to the phase changes in N₂ ice by virtue of the liberation or absorption of latent heat at the transition temperature. As the effect of latent heat on global temperature is small (6), we take the dependence of Triton's global temperature on time from the model of Brown and Kirk (8), in which the effect of the α - β phase transition is not included. The temperature distribution and heat flow in Triton's mantle are found in (8) by solving the heat conduction equation without phase changes for the underlying silicate and water-ice layers. We used the basal heat flow calculated in (8) as a lower boundary condition in our model.

Our main assumption is that Triton has permanent polar caps hundreds of meters thick. This agrees with the results of (8) for the case when there is no additional heat source on the core-mantle boundary in the northern hemisphere [compare with works of Hansen and Paige (7) and Spencer and Moore (6), based on a N_2 inventory no more than a hundred centimeters thick].

Seasonal temperature variations on Triton are driven by changes in Triton's subsolar latitude (Fig. 1), whose period is the least common multiple of Neptune's 165year orbital period and Triton's 688-year nodal precession period (12). Calculations (10) show that to a good approximation the seasonal temperature variations are quasiperiodic over a time period of ~1000 years. For simplicity we chose a period of 1000 years for our model runs. Diurnal temperature variations are small (5, 8) and are neglected. Seasonal sublimation (recon-

Fig. 1. Subsolar point on Triton. At Voyager 2 encounter the point was about -45° latitude and was moving further south to its extreme of about -52° densation) is neglected for the permanent N_2 deposits more than 150 m thick. There are two reasons for this. First, an after-the-fact estimation of the front speed gives a value of ~30 cm year⁻¹, which is much greater than the sublimation (recondensation) rate of ~1 cm year⁻¹ (2), so the α - β phase front always propagates much faster than the sublimation front. Second, the maximum seasonal sublimation (recondensation) layer is only about 10 m thick, which is much less than the N_2 layer thickness in our model.

We applied numerical methods to the heat transfer problem with phase changes in a two-dimensional domain (13, 14). The boundary separating the regions of cubic and hexagonal N_2 (there can be more than two regions) is isothermal, with a temperature U^* . The model is summarized as follows:

$$\rho(u,x,y)c(u,x,y)\frac{\partial u}{\partial \tau} = \operatorname{div}(\lambda(u,x,y)\nabla u), \text{ where}$$

$$u(x,y,\tau) \neq U^*,$$

$$u(x,y,0) = u_0(x,y), \qquad (1)$$

$$\frac{\partial u}{\partial x}\Big|_{x = 0} = \frac{\partial u}{\partial x}\Big|_{x = d_1} = 0,$$

$$\lambda \frac{\partial u}{\partial y} \bigg|_{y = d_2} = g,$$
$$u(x, 0, \tau) = \varphi(x, \tau).$$

Here *u* is temperature, λ is heat conductivity, *c* is heat capacity, ρ is density, and *g* is heat flow from the interior.

For a point P on the front defined by the surface $\Phi(x,y,\tau) = 0$, the two following equations are valid:

$$u(x,y,\tau) = U^*, \text{ and}$$
$$Q \frac{\partial \Phi}{\partial \tau} = (\lambda \nabla u|_{P+0} - \lambda \nabla u|_{P-0}) \cdot \nabla \Phi,$$



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where Q is latent heat per unit volume, P + 0 indicates a value taken on the α - β front approached from the β -N₂ region, and P - 0 indicates the same thing approached from the α -N₂ region.

It is known that the solution of problem 1, with an upper boundary condition $\varphi(x,\tau)$ periodic in time and an initial temperature u_0 which agrees with the boundary conditions at initial time, asymptomatically approaches the solution of the periodic problem. To solve the problem 1 numerically, the enthalpy method was used (15, 16). The temperature dependence of thermal characteristics along the equilibrium vapor pressure curve was taken from (11) and interpolated with polynomials (17).

Calculations were performed with the two-dimensional model for a periodic problem with a 1000-year period and the basal heat flow depending upon latitude. The dependence of the basal heat flow upon latitude (which was the largest two-dimensional influence in the problem) only minimally influenced the numerical solution for the case when there is no hot spot at Triton's core-mantle interface. This afterthe-fact finding made it possible (18, 19) to calculate temperature fields and the behavior of the phase fronts only for the maximum and minimum depths of 923 m (-90°) and 243 m (-57°) in the permanent N_2 southern polar cap, and the maximum and minimum depths of 911 m (+90°) and 157 m (+57°) in the permanent northern polar cap.

The maximum difference in depth between the corresponding phase fronts for layers with different thicknesses is only ~ 8 m, as in the cases of 157-m and 923-m N_2 layers. For a thinner layer (closer to the edge of the cap) the fronts propagate a few meters deeper. This can be explained by the unusual dependence of β -N₂ heat resistivity on temperature (11). The resistivity increases for $\alpha\text{-}N_2$ with rising temperature but drops for β -N₂ in the temperature interval between the phase transition point and the triple point (63.14 K). Because higher temperatures are reached at the base of the deeper layer (53.2 K at 923 m versus 39 K at 157 m) heat is conducted to the deepest phase front, thus buffering the cooling process and reducing the front penetration more for the thicker layer. A crucial role is played by the small influence of the basal heat flow (around 0.0033 W m⁻²) at the depth of interest on the front penetration.

The phase front pattern for all simulations of a permanent, solid N₂ layer having a thickness greater than 150 m is approximately the same because it is mostly influenced by the globally uniform surface temperature. The first front to appear on Figs. 2A and 2B is a β - to α -N₂ phase change front. Soon after the first front appears, a second front merges with it, forming confined regions of α -N₂ in the ambient β -N₂. At times there can be two separate phase fronts (Fig. 2). The first phase front penetrates as deep as 43 m. The α and β phases of N₂ are present on the surface for about the same total amount

of time during the 1000 years of the model run.

Our calculations indicate a strong phase stratification of the subsurface (Fig. 2). Laboratory experiments (12) show that the transition from less dense β to more dense α



Fig. 2. (**A**) The α - β fronts for a N₂ layer 923 m thick at the south pole. Plotted here is the depth of front penetration versus time. The plot represents a 1000-year period, where the initial time is at the Voyager 2 flyby (1989). The first front is marked by a solid line. The second front is marked by a dashed line. The regions of α - and β -N₂ are marked with letters. (**B**) The α - β fronts for a 157-m N₂ layer corresponding to +57° latitude (near the edge of the northern polar cap).

phase of N₂ causes extensive shattering of the crystals, so the N₂ ice layer on Triton is expected to have many scattering centers and thus an albedo much higher than that of non-fractured N₂. Nitrogen ice is bright if it is fractured on length scales of a few millimeters or larger, and it takes more than 10^6 years for fractures of this size to anneal (20). We conclude that permanent N₂ deposits, which undergo at least seven β to α phase transitions during the 1000 years modeled, are kept permanently fractured and therefore bright. This may explain why Triton's southern polar cap, though experiencing vigorous sublimation at the time of the Voyager flyby, had a surprisingly high albedo (~ 0.8).

Our results are almost symmetric for the northern and the southern hemispheres. If fresh nitrogen ice can form as a well annealed transparent layer on a seasonal time scale (20), the northern polar cap should have an albedo as high as that of the southern cap, provided it is composed primarily of N_2 (a 99% N_2 content in a mixture with three other components was deduced in (21) for a subsurface layer at least a few centimeters thick). During the Voyager flyby, latitudes northward of $+45^{\circ}$ were not observed because they were above the terminator, so we cannot test our hypothesis for the northern polar cap.

Using Brown's model (10) (which is not unique and in turn depends strongly upon the behavior of the subsolar point with time) for the recent temperature variations on Triton, we believe that before the Voyager flyby (1989), the surface N₂ in the caps had undergone the change from α to β phase. Thus α -N₂ existed on the surface of both polar caps during the ~70 years before the Voyager flyby, and the subsurface of the polar caps is now in the process of a transition from α to β phase (Fig. 2). We are making an additional assumption here that the approach of the phase boundary from the α phase is not disruptive for solid N₂.

In the low and middle northern latitudes, a lower albedo (~0.6) was seen by Voyager 2. This observation is consistent with the hypothesis (20) that a fresh, transparent, seasonal N2 layer overlies a dark substrate in these latitudes. The dark substrate is likely to be a lag deposit of organics produced by photon and charged particle bombardment of less volatile methane ice (22). If there is indeed a transparent layer of N2 in Triton's middle northern latitudes and northern equatorial regions, our model predicts that the layer will remain transparent (and thus the latitudes in question will remain relatively dark) until Triton's seasonal temperature again drops below the β - α transition temperature, at which point Triton's low to middle northern latitudes should brighten considerably.

Our model provides a mechanism to main-

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tain the permeable solid-state greenhouse underlayer required in the Kirk et al. (22) model of energy collection and transport for geyser-like plumes. Due to phase transition fracturing, permanent N₂ deposits are highly permeable. The transparent sealing overlayer for the solid-state greenhouse is provided by seasonal condensation if the initial grain size is less than ~ 1 μm (20). Here we assume that enough deposition has occurred on the southern polar cap since the last surface fracturing (according to our model it occurred around A.D. 1920) to produce a transparent layer and that enough time has passed without surface fracturing for initially bright fresh frost to evolve through sintering to a clear N_2 layer. To preserve a low permeability of the greenhouse overlayer (which is a few meters thick) we need to assume again that the approach of the phase boundary from the lower temperature does not disrupt solid N₂

The transparent layer could be considered as a super-greenhouse overlayer, whereas according to our model the permanent deposits beneath provide multiple fractures in which pressurized N_2 gas can collect and thereby supply geyser vent areas up to 1 km in radius. If this highly pressurized (due to the greenhouse heating) gas finds a vent in a sealing overlayer, it uses the fissures in the permanent deposits to be transported laterally toward the vent.

We hypothesize that geyser vent areas may be created when the impermeable capping overlayer is breached locally in the regions where contamination by CH₄ and CO is higher. Therefore, the phase transition temperature in these local regions is slightly increased in comparison with the less contaminated N2. These surface areas could be fractured a few years earlier than the ambient N₂ sealing layer, which remains intact until the global surface temperature drops to 35.61 K. This time interval, from our point of view, will help constrain the lifetime of geyser-like plumes. These speculations are valid only when Triton's surface temperature approaches the phase transition temperature from above.

Recent work by Tryka *et al.* (23) suggests that the 2.15- μ m absorption band in solid N₂ is sensitive to temperature and to the specific phase of N₂. The predicted variations in phase composition of Triton's permanent polar caps may reveal themselves in changes of the appearance and intensity of the 2.15- μ m N₂ absorption band as observed in ground-based spectrophotometry.

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and its approximation order is $O(h_x^2 + h_y^2 + \Delta \tau)$. An iterative method was used to solve the nonlinear discrete system at each time layer. The solution from the previous time step was chosen as an initial approximation for the iterative process. If the process does not converge at either half of the time step, then the time step is bisected.

- 17. A seventh-order polynomial was used to approximate density, second-order polynomials for the heat resistivity (the inverse of the heat conductivity), and third- and second-order polynomials for the α -N₂ and the β -N₂ heat capacity, respectively.
- 18. These speculations are valid only for the case when the upper boundary temperature is globally uniform and the media is homogeneous. Recent ground-based spectral observations of Triton's surface by Cruikshank *et al.* (19) showed that the content of methane in a mixture with N₂ is much less than 1%. The relative fraction of carbon monoxide to N₂ in an intimate mixture is believed to be 0.1% (19). The same relative fraction is derived in (19) for carbon dioxide, though it is more likely that carbon dioxide ice is segregated spatially, and can cover ~10% of the surface.
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Spectroscopic Determination of the Phase Composition and Temperature of Nitrogen Ice on Triton

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Laboratory spectra of the first overtone band (2.1480 micrometers, 4655.4 reciprocal centimeters) of solid nitrogen show additional structure at 2.1618 micrometers (4625.8 reciprocal centimeters) over a limited temperature range. The spectrum of Neptune's satellite Triton shows the nitrogen overtone band as well as the temperature-sensitive component. The temperature dependence of this band may be used in conjunction with ground-based observations of Triton as an independent means of determining the temperature of surface deposits of nitrogen ice. The surface temperature of Triton is found to be $38.0^{+2.0}_{-1.0}$ K, in agreement with previous temperature estimates and measurements. There is no spectral evidence for the presence of α -nitrogen on Triton's surface, indicating that there is less than 10 percent carbon monoxide in solid solution with the nitrogen on the surface.

The presence of molecular nitrogen (N_2) on the surface of Triton was identified from telescopic spectra obtained by Cruikshank

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et al. (1) on the basis of a weak absorption band at 2.148 μ m, although the physical state of the N₂ was unclear. The presence of N₂ was also deduced from emission lines in Triton's atmospheric spectrum seen by the ultraviolet (UV) spectrometer experiment on Voyager 2 during its 1989 flyby (2). Thermal measurements made by the Voyager infrared spectrometer indicated a surface temperature of 38^{+3}_{-4} K (3), and a surface pressure of 14 µbar was derived from measurements by the UV spectrometer (2). As the triple-point temperature of N₂ is

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