A SULFATE-RICH MODEL OF TITAN'S INTERIOR I: IMPLICATIONS FOR THE COMPOSITION OF CRYOMAGMAS.

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Introduction: The existing paradigm regarding the internal structure of Titan consists of a rocky core overlain by an icy mantle bearing a deep underground ocean of aqueous ammonia [e.g., ref. 1]. Speculation regarding the possibility of cryovolcanic activity on Titan [2], which is now apparently being borne out, has focused upon aqueous ammonia as the likely cryomagma. Measurements of the viscosity of ammonia-water mixtures have been used to infer that cryovolcanoes and flows on Titan will resemble terrestrial basaltic analogues [3]. Indeed, the best candidate volcanic edifice, Ganesa Macula and its associated flow deposits, bear comparison with basaltic deposits elsewhere in the solar system [4]. However, the initial quantity of ammonia within Titan is not well known, values ranging between 18 wt % of the icy component [5] to essentially zero [6]. The present paradigm also overlooks the plausible interaction between the volatile fraction of Titan and the water soluble components (mostly sulfates) in the chondritic core during differentiation, as explored by Kargel for the Jovian moons [7].

Here, we consider the consequences of extending Kargel's model for the Galilean moons, involving the leaching of sulfates from a chondritic core, to a satellite containing ammonia.

A new internal structure for Titan: We assume that a chondritic core yields up 10 wt % of sulfates (mostly $MgSO_4$) that are free to go into solution in the liquid volatile component of the early satellite. This volatile component consists of water, ammonia and methane, and we fix $NH_3:CH_4 = 1$ for simplicity. Soluble sulfates in solution react with ammonia and water to form soluble ammonium sulfate and insoluble hydroxides. The present mass and density of Titan can be reproduced from an initial rock mass fraction of 0.82; an ammonia abundance of 12.7 wt % in the volatile fraction leads to complete consumption of NH_3. Models of the ammonia abundance inside Titan vary from 1 – 18 wt %, of which a large fraction may have been converted to N_2 and lost from the atmosphere early in Titan's history. Thus it is reasonable to hypothesise that all of Titan's primordial ammonia may have reacted with sulfates to form ammonium sulfate.

Titan's model internal structure following differentiation consists of a chondritic core of radius 1990 km overlain by a deep liquid mantle consisting of an aqueous solution of ammonium sulfate and dissolved methane at saturation throughout the water column; insoluble hydroxides have precipitated out to form a sediment layer ~ 40 km thick at the base of the ocean. Titan also has a hot thick atmosphere of nitrogen (formed by dissociation of ammonia) and the vast majority of Titan's methane inventory. Upon cooling, dissolved methane in the ocean forms a solid crystalline clathrate. In the upper half of the water column the pressure is low enough to form a stable structure I clathrate (having a guest:host ratio of 1:5.75), which floats to form a crust. In the lower half of the water column, the pressure is high enough to form the high-pressure clathrate polymorph MH-II (guest:host ratio = 1:3.5), which will also float upwards, presumably transforming to MH-I nearer the surface and expelling excess methane. The final methane clathrate crust thickness is ~150 km. Macro-porous clathrate grains will carry pockets of ammonium sulfate solution upwards and incorporate them into the crust, where they will ultimately solidify to ice + ammonium sulfate tetrahydrate (AST) [8]. During the formation and growth of the crust, we would expect major melt throughs due to thermal plumes and and impact events, as well as local thermally-, compositionally-, or tidally-driven volcanism, to emplace large volumes of aqueous ammonium sulfate at the surface and within the crust. Underneath the crust, the aqueous ammonium sulfate ocean (which is almost at its eutectic) will initially precipitate high-pressure ice VI as it cools further. This will sink and accumulate on the ocean floor (as a layer a few tens of kilometers thick), driving the composition of the residual liquid towards the binary eutectic at 40 wt % $(NH_4)_2SO_4$ (at ambient pressure). Additional clathrate will crystallize as the oceanic salinity increases towards the eutectic, lowering the methane solubility. Although we have not done detailed thermal evolution modeling of this scenario, it is quite plausible that the ocean of eutectic ASS approximately 375 km deep persists to the present day, in which case it will be detectable from the tidal variation of Titan's quadrupole moments [e.g., ref. 9]. If the ocean has crystallized, it will consist of a mixture of ices II, V and VI and AST (and possible high-pressure polymorphs of AST).

The subsurface ocean (if it exists) is probably too dense for liquids to be extruded through the crust, without invoking an unfeasible volatile content, or tidal pumping [10]. However, the AST + ice intrusions permeating the crust can be partially melted to yield aqueous ammonium sulfate magma. The volume change on melting (we estimate ~1.5 %) will generate an overpressure in the melt source of perhaps several tens of MPa, capable of forming cracks in the brittle crust and pumping magma towards the surface. Moreover, contact between the magma and wall rock (methane clathrate) will allow some methane to dissolve in the magma, as well as eroding fragments of wall-rock that can be transported as xenoliths. Upon rising to the clathrate decomposition depth (at 270 K, MH-I decomposes at 26 bar, corresponding to a depth of ~2000 m), the entrained xenoliths will break down to ice + methane gas, powering highly explosive eruptions (see companion abstract [11]) with lava fountains up to several kilometers high.

Discussion: There have been no high pressure studies of the $(NH_4)_2SO_4 - H_2O$ system; indeed, virtually nothing is known about even the ambient pressure tetrahydrate phase. However, comparison with the $MgSO_4 - H_2O$ system at high pressure [12] suggests that the eutectic melting temperature will reach a minimum where AST is in equilibrium with ice III (at 2 – 3 kbars, or 150 – 225 km depth). Given the very low thermal conductivity of methane clathrate [13], the estimated heat flow [14] may result in a thermal gradient of 10 K km^{-1} (compare 2.5 K km^{-1} for an ice Ih crust). Thus, the ambient-pressure eutectic melting temperature can be reached at a depth of just 16 km. Melt pockets could be carried up to the base of the brittle lithosphere by convection cells in the lower portion of the clathrate shell.

Sulfate solutions will have a much lower viscosity compared to aqueous ammonia [3], and are erupted at a higher temperature (~270 K). Although we do not know how ammonium sulfate solutions will behave when quenched, we know from our own laboratory experience that supersaturated magnesium sulfate solutions crystallize rather than forming glasses when quenched from room temperature in liquid nitrogen (i.e., at very high rates of > 50 K s^{-1}): we have found that aqueous ammonia solutions form glasses even when cooled at rates of 0.01 K s^{-1}. The combination of low eruption viscosity, high eruption temperature, and an ability to crystallize even when quenched very rapidly (thus providing latent heat of crystallization to the flow) means that ammonium sulfate cryomagmas *might* be a more attractive proposition for explaining the very long (ca. 100 km) flow features at Ganesa Macula.

We predict here, and in our companion abstract [11], that Titan has been extensively resurfaced by lavas composed of aqueous ammonium sulfate, and by huge quantities of easily eroded cryotephra consisting of ice and ammonium sulfate (or its tetrahydrate). Given the very large difference in density between ice and ammonium sulfate ($\rho = 1770$ kg m^{-3}), both fluvial and aeolian processes will very effectively separate the two minerals. Thus, we should expect ammonium sulfate to form the major lag deposit on the higher terrain (and the first airfall from cryoclastic clouds), whereas ice should be more easily transported to lowland basins; more so in the case of possible highly vesicular icy scoria or pumice.

The diffuse near infrared reflection spectrum of ammonium sulfate [15] is similar to that of ice and of other hydrated sulfate salts, and is a credible candidate for the unidentified component of the surface spectrum at the Huygens landing site [16]. Although the reflection spectrum of ammonium sulfate in the mid-infrared appears not to have been measured, the transmission spectrum exhibits no absorption features at 5 μm (whereas the reflectance of ice is roughly 3 % at this wavelength [17]), also making it a viable candidate for the 5 μm bright spot (associated with the feature provisionally named Hotei Arcus) described by Barnes *et al.* [18]

Finally, a warm ammonium-rich subsurface ocean is a considerably more attractive environment for life than the previously mooted aqueous ammonia ocean [19]. Indeed, organisms could survive in pore fluids or grain-boundary fluids to within a few tens of kilometres of the surface.

References: [1] Tobie *et al.* (2005) *Icarus* **175**, 496-502. [2] Kargel, J. S. (1992) *Icarus* **100**, 556-574: Lorenz, R. D. (1996*) Planet. Space Sci.* **44**(9), 1021-1028. [3] Kargel, J. S., *et al.*, (1991) *Icarus* **89**, 93-122. [4] Lopes, R., *et al.* (in prep). [5] Hunten, D. M. *et a*l. (1984) In, *Saturn*. University of Arizona Press, 671-759. [6] Mousis, O., *et al.*, (2002) *Icarus* **156**, 162-175. [7] Kargel, J. S. (1991) *Icarus* **94**, 369-390. [8] Xu, J., *et al.,* (1998): *J. Phys. Chem. B* **102**, 7462-7469. [9] Rappaport, N., *et al.,* (1997) *Icarus* **126**, 313-323: Castillo, J., *et al*., (2002) *LPSC* **33**, abstract 1989. [10] Mitri, G., *et al*., AGU, Fall Meeting, abstract #P44A-07 (2005) [11] Grindrod, P. M. and Fortes, A. D. (2006) *LPSC* **37**. [12] Hogenboom, D. L., *et al.* (1995) *Icarus* **115**, 258-277. [13] Krivchikov, A. I. *et al.*, (2005) *J. Low Temp. Phys.* **139**, 693-702. [14] Sohl, F., *et al.,* (1995) *Icarus* **115**, 278-294. [15] Clark, R., *et al.* (2003) USGS Digital Spectral Library, USGS Open File Report 03-395. [16] Tomasko, M., *et al.,* (2005) *Nature* (doi:10.1038/nature04126). [17] Salisbury, J. W. *et al*., *J. Geophys. Res*. **99**(B12), 24235-24240. [18] Barnes, J., *et al*., (2005) *Science* **310**, 92-95. [19] Fortes, A. D. (2000) *Icarus* **146**, 444-452.

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