ERUPTION OF AMMONIA-WATER CRYOMAGMAS ON TITAN 1: CRYSTALLISATION AND COOLING DURING ASCENT. K. L. Mitchell^{1,2}, J. S. Kargel³, R. M. C. Lopes¹, J. Lunine^{4,5}, G. Mitri⁴, R. Lorenz⁴, N. Petford⁶ and L. Wilson², ¹Jet Propulsion Laboratory, Mail Stop 183-601, 4800 Oak Grove Dr., Pasadena, CA 91109, *Karl.L.Mitchell@jpl.nasa.gov*, ²Environmental Sci. Dept., Lancaster Univ., UK, ³Univ. Arizona, Dept. of Hydrology and Water Resources, Tucson AZ, ⁴Univ. Arizona, Lunar and Planetary Lab., Tucson AZ, ⁵Institute Nazionale di Astrofisica, Roma, Italia, ⁶School of Earth Sciences and Geography Kingston University, London, UK.

Introduction: Several cryovolcanic landforms have been interpreted on Titan, indicating a broad range of eruption styles and rheological properties [1,2]. We are developing a semi-analytical model for the ascent of methane-expansion driven ammoniawater cryomagmas on Titan, based upon a silicate magmatic conduit flow model [3]. Some preliminary results are presented based on thermodynamic analysis. The degree of crystallisation of the magma is strongly controlled by the starting depth/pressure. The range of different crystal fractions may help to explain the range of apparent rheological properties inferred for surface features [2].

Thermochemistry: We consider ammonia-water solutions [4] with initial ammonia concentrations <32 wt% (ammonia dihydrate peritectic), consistent with a very water-rich bulk composition dictated by cosmochemical and orbital evolution considerations [6]. The negative buoyancy of most ammonia-water magmas (except dihydrate compositions near the eutectic) may be overcome, as the overpressure for refreezing $(10^7 10^8$ Pa) in magma chambers exceeds the lithostatic pressure required to cause a surface eruption by large driving pressures [6]. Crustal density may also be greater than that of pure water-ice, as a result of meteoroid impacts, although this effect may be offset by near-surface fracturing and porosity. However, we consider it likely that magma ascent is driven by the expansion of methane during decompression, because methane is seen in abundance in Titan's atmosphere, was detected on the surface by the Huygens probe [7] and has appropriate volatility under relevant conditions. Exsolution of methane from the cryomagma is not modelled, due to the lack of a treatment for solubility in, and latent heat of exsolution from, ammoniawater mixtures; we treat only the behaviour of methane after its exsolution. We do not as yet consider the possibility of cryomagmas composed of sulphates [8]. organics such as methanol (e.g. [9]) or volatiles other than methane such as ethane, as currently-available thermochemical data is insufficient and no increase in model complexity is justified by the data.

The eruptants are considered to be Newtonian and 3-phase: solid water Ice-I (H₂O), liquid ammonia hydrates $(NH_3)_x(H_2O)_{(1-x)}$ and gaseous/supercritical methane (CH₄). Liquid and solid phases are assumed to be incompressible, and the methane is treated as an ideal

gas, which provides a good first order fit over the pressures considered. Mixture viscosity is derived based on empirical data [9], modified to take into account the effect of solid crystals using a method [10] based on the lubrication limit concept of particle interactions. Solid fraction (we assume freezing out of ice forms crystals rather than glasses) is determined using the ammonia-water equation of state ([11] summarized in Fig. 1). Freezing of pure water-ice during decompression and cooling will drive the cryomagma to more ammonia-rich concentrations. If energy is extracted faster than water freezes then it is driven toward the eutectic between ice and ammonia dihydrate, which is shifting to higher ammonia concentrations above peritectic temperatures.



Fig. 1: Liquidus for ammonia hydrates at sub-perifectic concentrations of ammonia for a range of pressures. Source: [11].

Dynamics: Decompression and ascent of the cryomagma under adiabatic conditions results in temperature and phase changes according to the relation (from conservation of energy, after [3]):

$$c dT = h_{\text{H2O,fusion}} \delta m_{\text{s}} - (m_{\text{m}} / \rho_{\text{m}}) dP - u du - g dz$$
 (1),

where *c* is the bulk specific heat capacity of the eruptants, *T* is the temperature, $h_{\rm H2O,fusion}$ is the latent heat of fusion of ice, $m_{\rm s}$ is the mass fraction in ice, $m_{\rm m}$ is the mass fraction of the cryomagma (solid + liquid) and $\rho_{\rm m}$ is its density, *P* is the bulk pressure, *u* is the ascent velocity, *g* is the surface gravity, and *z* is the elevation. The physical meaning of the second expression on the right-hand-side of (1) might not be immediately obvious; combined with *u* d*u* it represents an amalgamation of viscous dissipation and gas expansion.

Analysis: Solution of (1) reveals that adiabatic temperature changes during ascent are generally small

(typically a few K), even when from a great depth. The 2^{nd} and 4^{th} expressions of (1) are almost equivalent, and so, assuming a pure water-ice crust ($\rho_c \sim 920$ kg m⁻³), rates of temperature loss are <0.01 K/km, primarily due the need to overcome negative buoyancy. Titan's geothermal gradient is estimated to be ~1-2.5 K/km, and so eruptions sourced from reservoirs in the crust that have time to cool to ambient temperatures will generally erupt at much lower temperatures than given above. The kinetic energy term $(u \, du)$ has a small effect on temperature unless eruption speeds are very fast (>> 50 m s⁻¹), which is only likely if activity is highly explosive. Any cumulative temperature drops may also be partly buffered by latent heat of crystallisation of water. Crystallisation or glassification, therefore, will mostly be due to decompression. Increase in ammonia concentration can be inferred directly from Fig. 1, and crystallization fraction is unity minus the ratio of starting and finishing concentrations.

Mitri et al. [6] propose that cryovolcanic processes are related to bottom crevasse formation in an ice shell floating on an ammonia-water ocean (at ~70 km, interface temperature ~244 K), transport of ammonia-water pockets to the base of the stagnant lid by convective motions in the ice, refreezing of chambers of ammonia-water at the base of the stagnant lid. Moreover, the formation of chambers can occur at a depth of the order of kms from the surface, consistent with interpretations of calderas in SAR imagery [1,2]. Note that for the cryomagma chemistries being considered, formation of shallow magma chambers is only likely if the melt is near-eutectic ammonia dyhydrate, or if the crust contains a significant fraction of denser materials (e.g. iron or silicate delivered by impactors); otherwise the magma will be negatively buoyant. Negative buoyancy effects are further enhanced near the surface due to increased impact fracturing and porosity, and so either source overpressure or driving volatile expansion is probably necessary for cryomagmatic eruptions.

Eutectic starting concentrations are assumed, as eruption initialization is probably caused by overpressure resulting from ice-crystal growth [6]. We find that the degree of crystallisation during ascent is disproportionately greater from a greater depths. We consider two end-member scenarios, inspired by [6]: (1) A deep eruption from a bottom crevasse sourced from a magma ocean, (2) A shallow eruption from a near-surface magma chamber.

Deep eruptions. Eruptions directly from an ammonia-water ocean [6] represent the deepest plausible magma source. Assuming a pure water-ice crust we get a starting pressure at 70 km of ~91 MPa. Given NH_3 starting concentrations at the eutectic (~13 wt%)

at this pressure, the process of decompression and cooling would result in ice crystallisation of ~30 wt%, a final cryomagma NH₃ concetration of ~18.5 wt%, and an ~9× increase in bulk viscosity. The final crystal fraction could be increased significantly if the pressure at depth were greater. A 200 MPa reservoir, for example, could result in crystallization of ~60 wt%, and an ~80× increase in bulk viscosity.

Eruptions from shallow magma chambers. Crystallisation during adiabatic ascent is minimal (just a few wt%). However, initial indications are that the erupted materials associated with apparent calderas can have a considerable yield strength [2], inconsistent with ammonia-water mixtures with small crystal fractions. Five possible explanations exist: (1) crystallisation occurred within the magma chamber, (2) crystallisation occurred after eruption, (3) the eruption was sufficiently slow that the magma cooled during ascent due to loss of heat through conduit walls, (4) the chemistry is not pure ammonia-water (e.g. methanol [9]), and (5) the magmas did not erupt from shallow magma chambers.

Discussion: Our model indicates that methanedriven ammonia-water eruptions are possible on Titan, but this does not exclude other chemistries, which were not explored here. The eutectic starting concentration assumption is questionable. Equilibrium crystallization may also be suspect, as supersaturation can occur in both silicates and cryomagmas. However, as this is difficult to sustain over long timescales, we consider its effect is likely to be small. A more critical limitation of the method described is if ammonia concentrations are so high that the local temperature is above the eutectic. Starting temperatures are also likely to be elevated relative to the ambient geothermal gradient when erupted from crustal reservoirs, as the process of partial freezing due to cooling is a viable initiator for cryovolcanic eruptions. Further theoretical chemistry and/or laboratory work will be necessary to produce a more rigorous analysis of likely styles of cryovolcanic eruptions over a range of compositions.

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