CLATHRATE FORMATION IN THE NEAR-SURFACE ENVIRONMENT OF TITAN.

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Introduction: In terrestrial near-surface environments, alteration of rocks and sediments is mediated by water, producing hydrous minerals: we need not be concerned about water being consumed in this fashion since the Earth has plenty more in the oceans. On Titan, the liquid mediating alteration of the bedrock and regolith may be a mixture of light hydrocarbons - ethane and methane - the alteration product being the well-known inclusion compound known as a clathrate hydrate. Formation of hydrocarbon clathrates may be a concern for understanding the source of Titan's atmospheric methane, since recent Cassini data of Titan appear to indicate that there is not a vast abundance of liquid hydrocarbons (i.e., oceans) at the surface. Here, we briefly consider the formation not only of hydrocarbon clathrates but of air clathrates in the near surface environment of Titan.

Hydrocarbon clathrates: It is apparent from Cassini ISS [1], VIMS [2] and RADAR [3] observations, that there are not widespread bodies (large seas or oceans) of liquid hydrocarbons (ethane/methane) at Titan’s surface, as had been expected; there do not even appear to be large crater lakes. However, the existence of liquids contained in crustal pore spaces – a so-called ‘methanifer’ – remains a viable hypothesis [4]. By analogy with the Earth’s moon, we might expect Titan to possess an impact shattered mega-regolith extending to depths of a few kilometres, providing ample pore space to conceal large volumes of liquid hydrocarbons. Assuming a typical thermal gradient in the crust of ~5 K km^{-1} means that the boiling point of pure methane (111 K) occurs at a depth of just 3 km, and of pure ethane (189 K) at ~20 km. Thus liquid hydrocarbons are likely confined to the upper 10-15 km of the crust and are actively circulating. Upwelling of warm ice, or liquid water, would vigorously boil these hydrocarbons, perhaps driving explosive geysering events. Consider, for example, a pluton of liquid water intruded into the upper crust at a depth of 5 km, and buffered at 273 K by the release of latent heat of crystallisation; the thermal gradient in the overlying crust is locally ~36 K km^{-1}, meaning that even pure ethane will boil at depths of just 2.6 km. However, ethane-rich liquids in contact with ice at low temperatures and elevated pressures (at 3 km depth, the hydrostatic pressure is ~ 400 bar) will form structure I clathrate hydrates (guest:host ratio = 1:5.75); methane-rich mixtures form structure II clathrates (guest:host ratio = 1:17) [5]. Indeed, ethane-bearing clathrates are stable at lower pressures and higher temperatures than pure methane clathrates [6]. The formation of these clathrates will not clog up available pore spaces since the clathrates form by diffusion *into* the surrounding ice, but they will prevent liquid hydrocarbons from being able to resupply photolysed methane lost from the upper atmosphere. Formation of extensive clathrate deposits in the crust may also significantly change the thermal gradient in the crust, since clathrate hydrates are known to have thermal conductivities an order of magnitude lower than water ice [7].

If liquid hydrocarbons in the near surface environment of Titan do become locked up in clathrates, then the question remains as to the resupply mechanism for the atmospheric methane inventory. Breakdown of methane clathrates in Titan’s deep mantle appears unlikely, as CH_4 clathrates have been shown recently not to be decomposed by pressure but instead form high-pressure polymorphs (which are, in fact, even more CH_4-rich) [8]. Remaining hypotheses include CH_4 production by methanogens in a subsurface ocean [9], and exogenic delivery by cometary impacts [10]: impactors could also dissociate any local clathrates in the target rocks, but the extensive hydrothermal systems likely to form under the new crater will favour the recrystallisation of clathrate hydrates. It is also a plausible hypothesis, though difficult to test at present, that Titan’s atmospheric methane, its apparently young surface, and large orbital eccentricity, are the result of a geologically recent catastrophe.

Nitrogen clathrates: Another possible source of active clathrate formation is at the surface. Cassini RADAR images appear to show lobate features which may be cryovolcanic flows [11], consisting perhaps of pure water, or some solution containing ammonia and/or methane. Watery fluids that are erupted onto the surface of Titan will experience rapid cooling at the air-water interface from contact with very cold (90 K) nitrogen gas. If chemical interaction with the atmosphere is ignored, one would expect water ice to crystallise and form a crust. However, at a pressure of 1.5 bar, N_2-clathrate could form directly at the air-water interface at temperatures below 160 K [12], or may form by the reaction of N_2 with a relatively warm ice crust. The latter process occurs by the initial formation of a thin porous clathrate rind, followed by diffusion-limited growth into the ice [13]. Data on the kinetics of these processes do not exist at such low temperatures and low N_2 fugacities; however one can presume that the reaction, whilst very slow in the laboratory, will proceed quickly on geological timescales. If it is assumed that 10% of Titan's heat flow, taken to be ~$5x10^{11}$ W [14], is used in melting of ammonia hydrates (heat of fusion ~150 J g^{-1}), and that ~20% of this makes it to the surface, then the mass of erupted melt is $6.6x10^4$ kg s^{-1} ($2x10^{12}$ kg yr^{-1}). Even if only 10% of the erupted liquid is converted to N_2-clathrate, and the cage-filling efficiency under 1.5 bar of N_2 is just 5%, then the total mass of N_2 clathrated over 4.5 Ga is $1.3x10^{19}$kg; *this is equivalent to the quantity of N_2 in the present atmosphere*. Thus, if Titan were indeed being actively resurfaced by cryovolcanism, this mechanism could consume a large quantity of atmospheric nitrogen.

Summary: Formation of hydrocarbon and air clathrates on Titan may be an active process which affects models of atmospheric evolution. Presently, little is known about the kinetics of clathrate formation, particularly at low temperatures and gas fugacities; certainly further research in this area is warranted. It is unlikely that the spectral signature of clathrated N_2 or CH_4 molecules will be detectable through an atmosphere containing both species; detection of clathrates may require in situ sampling of the surface.

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