

## CAN WE RADIOMETRICALLY DATE CRYOVOLCANIC FLOWS ON ICY SATELLITES?

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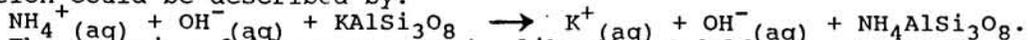
It is commonly assumed that radiometric dating of natural rocks and minerals is practical with silicate substances, but will not be possible with cryovolcanic ices on the icy satellites of the giant outer planets because of the presumed lack of high atomic weight radioactive and radiogenic elements in the ices. If true, this would seriously hinder our future efforts to understand the geological and cosmogonic histories of the icy satellites. This report is a preliminary assessment of the potential for obtaining absolute ages; the view from this lab is rather encouraging, if only we can obtain some samples!

We might be able to apply K-Ar methods of dating using degassed or partially degassed silicate xenoliths, such as certain phyllosilicates. A big problem frequently encountered in terrestrial K-Ar and Ar-Ar dating of clays and certain very fine-grained micas is that many of these (e.g. glauconite) readily lose their radiogenic Ar and even exchange Sr at Earth surface temperatures in the presence of fluids. This "problem" may be of great utility in dating icy satellite surfaces if some xenolithic phases tend to equilibrate with their surroundings at satellite interior temperatures, but then retain their radiogenic Ar at satellite surface temperatures. If so, the K-Ar isochron and  $^{40}\text{Ar}/^{39}\text{Ar}$  step heating methods applied to xenolithic silicates transported to the satellite surfaces may yield absolute cooling ages for the flows. However, beyond the many technical uncertainties at this point, these methods of dating will require the good fortune of sampling appropriate siliceous xenoliths, which may or may not be widely dispersed in cryovolcanic flows. Other dating techniques involving cosmogenic nuclide production (e.g.  $^{14}\text{C}$  and  $^{10}\text{Be}$ ) may turn out to be useful for dating very young cryovolcanic flows or pyroclastic deposits as may occur on Enceladus and Europa.

Other more conventional dating schemes rely on the presence of radioactive elements dissolved in the liquid at the time of eruption. Natural aqueous substances on Earth (river water, seawater, and hydrothermal fluids) contain plentiful dissolved salts, including the same elements used for radiometric dating of rocks. Clearly, water is a powerful leaching agent for temperatures near 300K. Additionally, the occurrence of water-soluble salts in carbonaceous chondrites indicate that processes of aqueous alteration, transport, and re-precipitation have occurred in some meteorite parent bodies. These considerations suggest that aqueous cryovolcanic liquids, believed to have been a chief geological re-surfacing agent on icy satellites, would also have contained dissolved salts leached from the silicate portions of these objects.

However, there are two important considerations which do not allow one to so quickly draw this conclusion: first, most common cryovolcanic lavas probably are ammonia-water-rich (but note that ammonia-water solutions are widely utilized in the mining industry as a leaching agent). Secondly, the ammoniacal aqueous cryo-lavas are probably generated by partial melting near the ammonia-water peritectic ( $-97^{\circ}\text{C}$ ), and the low temperatures generally should reduce salt solubilities, and may considerably affect the kinetics of the leaching reactions. The remainder of this report focusses on the solubility of potassium salts in ammonia-water liquids, determined in this lab experimentally.

If pure ammonia-water liquid was the reactive leaching agent, and if feldspar was the host phase for K in unaltered silicates, the chemical exchange reaction could be described by:



The ammonium feldspar component, like the K-feldspar component, may reside in solid solution in plagioclase, although several terrestrial hydrothermal deposits include a nearly pure ammonium end-member, buddingtonite, believed to have been formed by the low temperature (ca. 300K) reaction of plagioclase with ammonium-rich fluids (1). If this were the only important exchange reaction, then the leached K would exist in solution as dissolved KOH, which is highly soluble in the ammonia-water peritectic liquid. However, the likely presence of other ionic species in solution, including  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Na}^+$ , and  $\text{NH}_4^+$ , requires one to consider equilibria involving many different salts.

The approach used here is to simplify the chemistry to 3 and 4-component systems. Early experimental runs have indicated that several carbonate and sulfate salts have very low solubilities in the ammonia-water peritectic liquid (2); on the one hand, these low solubilities suggest that these salts will be early crystallizing phases in solidifying cryolavas; on the other hand, their

low abundances indicate that they may be insignificant with respect to K salt precipitation. Therefore, the first step toward chemical simplification is to ignore the sulfates and carbonates. And, the extremely high solubility of KOH indicates that KOH hydrate will never attain saturation. Some of the chlorides have intermediate solubilities, suggesting that these may be the most important salts in ammonia-water cryolavas.

Figure 1 shows the liquidus surface for the ternary system  $\text{H}_2\text{O}-\text{NH}_3-\text{NaCl}$ . The rather high solubility of the halite component (NaCl) in the peritectic liquid (13%) makes hydrohalite ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ) unlikely to be near saturation in freshly erupted liquids. However, hydrohalite will probably be an important late-stage crystallization product along with other minor constituents and the dominant ammonia hydrates. The radioactive elements  $^{40}\text{K}$  and  $^{87}\text{Rb}$  do not substitute for Na significantly in halite structures at low temperatures; instead, K and Rb probably enter together into sylvite ( $\text{KCl}-\text{RbCl}$  solid solution) (3). Figure 2 shows the liquidus surface of the system  $\text{H}_2\text{O}-\text{NH}_3-\text{KCl}$ ; note that the KCl concentration in the ternary peritectic liquid is substantially lower than is the case with NaCl (0.65% vs. 13 weight %). The importance of NaCl with regards to KCl precipitation is the solubility moderation exerted by the common ion effect. A simple calculation shows that KCl solubility in the hydrohalite-saturated ammonia-water peritectic liquid will be reduced to about 0.03% (= 150 ppm of K). It seems likely that the progressive concentration of NaCl in the residual liquid of solidifying flows will force the precipitation of sylvite. The likely widely distributed occurrence of sylvite in at least minor quantities provides for the future possibility that sylvite can be separated from returned samples and can be dated by the K-Ar and Rb-Sr mineral isochron methods. On the other hand, KCl solubility is high enough that "whole-rock" samples may contain enough K to permit whole-rock K-Ar dating, which might be accomplished *in situ*. Alternatively, or additionally, K and Rb may precipitate in other salts not yet considered, such as carnallite ( $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$ ), schoenite ( $\text{K}_2\text{SO}_4\cdot \text{MgSO}_4\cdot 6\text{H}_2\text{O}$ ), or in ammonium salts by the replacement of  $\text{NH}_4^+$  (the ionic radii of  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{NH}_4^+$  are nearly identical).

It must be emphasized that these experimental studies and the comments pertaining to them ignore possible kinetic limitations on leaching at low temperatures. This deficit as well as the possibilities offered by additional salt components are being addressed by further work.

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2. Kargel, J.S., 1988, *Lun. Planet. Sci.*, XIX, 583.
3. Hovi, V., 1950, *Suomen Kemistilehti*, 232, 80.

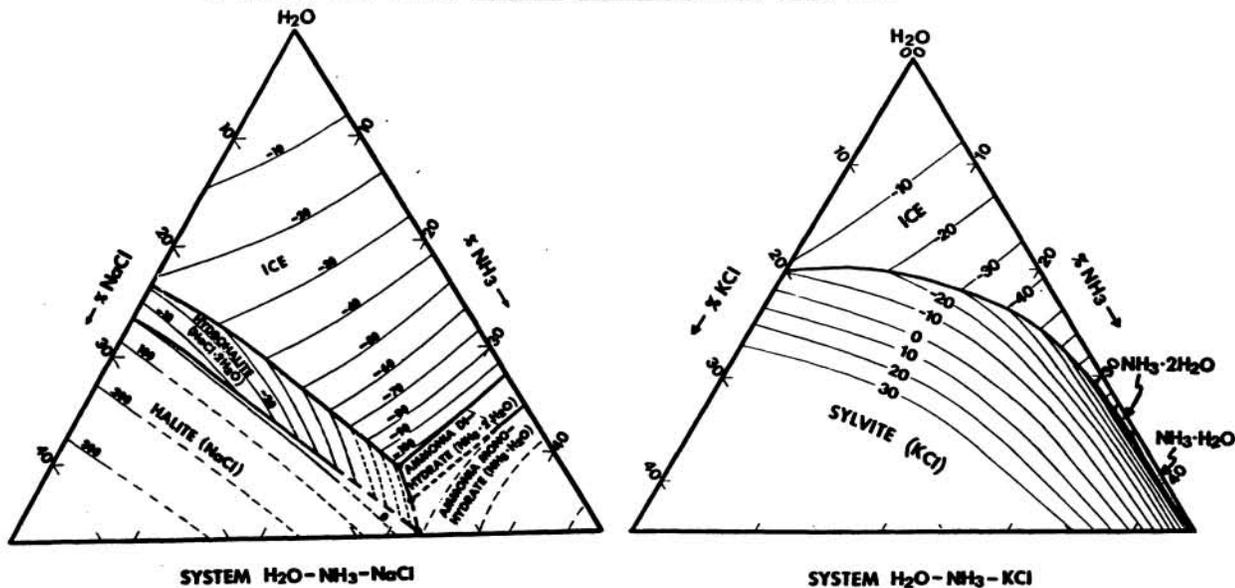


Figure 1. Liquidus surface in the ammonia-water-sodium chloride system. Isotherms give liquidus temperature in  $^{\circ}\text{C}$ , and are dashed where extrapolated.

Figure 2. Liquidus surface in the ammonia-water-potassium chloride system.