

Chloromethane Clathrate on Mars?. A. Steele¹ L.G. Benning², R. Wirth², M. Fries³. ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd, Washington DC 20015. asteel@carnegiescience.edu
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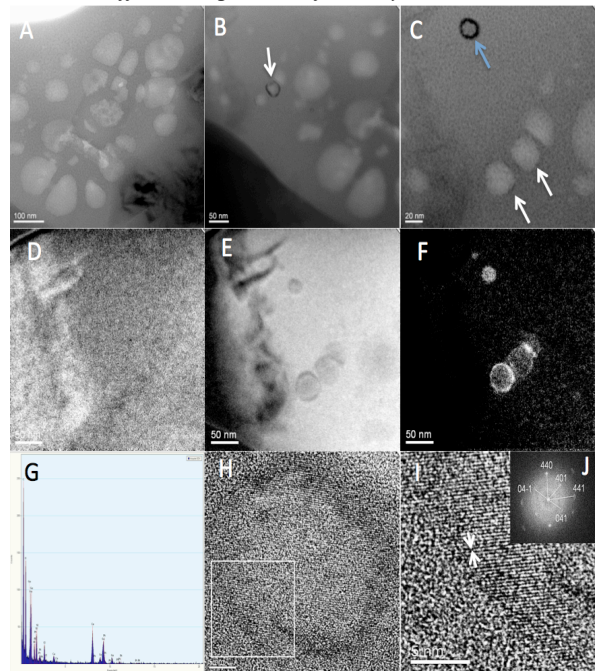
Introduction:

The discovery by Viking of chloromethane and dichloromethane on Mars was initially dismissed as contamination from cleaning fluids (1). However, recently the Sample Analysis at Mars instrument onboard the Curiosity rover discovered chloromethane, dichloromethane, trichloromethane, chloropropane and chlorobenzene on Mars (2). Research on Mars meteorites has shown the presence of a native, refractory macromolecular carbon (MMC) phase in 13 meteorites studied (3). This work essentially combines these two sets of observations to show that nanocrystallites of a chlorohydrocarbon are intimately linked to vesicles within a MMC phase in NWA1950. Transmission electron microscopy of these C, O and Cl rich crystallites reveals three possibilities, a type I or II clathrate hydrate structure or phosgene (Figure 1). Given the formation conditions of these phases we conclude that the crystallites are probably chlorohydrocarbon, CO₂ containing, clathrate hydrate. These results combined reveal the presence of a chloromethane clathrate like phase inside the macromolecular carbon that is undoubtedly Martian in origin.

While phosgene and di and trichloromethane / CO₂ mixed clathrates fit the elemental data, lattice parameters and angles found in TEM, we are inclined to rule out the crystallites as being pure phosgene as the melt ing point of phosgene is -128°C and so this crystallite should have dissociated under terrestrial temperature conditions. However, the mixed chloromethane / CO₂ clathrate hydrates studied by Stackelberg (1949) were found to be stable at temperatures well above 0°C (4). More recent studies on chloromethane clathrates have also shown that these phases can be stable to greater than room temperatures (5,6). Furthermore, several studies have shown that clathrates can be stable at far higher temperatures than initially postulated due to a phenomena known as anomalous preservation (7). Given these constraints and the diffraction data that shows the crystalline phase has either a 17.2 Å unit cell indicative of a type 2 clathrate hydrate or a 15.2 Å unit cell indicative of a type 1 clathrate hydrate it seems more likely that the crystallites represent a type 2, chlorocarbon clathrate hydrate that is stabilized by either CO₂ (most likely), H₂ or O₂ (5,6).

Figure 1: shows the results of TEM analysis of the area shown in Figure 2. *A*) is a higher magnification of the vesicular area showing the distribution and shape of the vesicles within the carbon rich phase. *B*) shows the presence of a small 30nm diameter crystallite

trapped in the carbon rich phase (marked by an arrow), *C*) shows the presence of a 20nm diameter crystallite also trapped in the carbon rich phase (dark arrow) and also the presence of crystalline fringes around the edge of some of the bigger vesicles (lighter arrows). *Figure D-F* are the results of EDS mapping of the area shown in *Figure 3C* and reveal that the crystallites are oxygen, carbon and chlorine rich. *G*) is an EDS spectra of the crystallite shown by the dark arrow in *Figure 3C* showing C, O and Cl within the crystal. *H*) shows a high resolution light field TEM image of the whole crystallite showing the presence of lattice fringes. *I*) reveals that the spacing between the lattice fringes is easily measurable (see arrows) and inset *J*) shows the FFT of the whole crystallite revealing the electron diffraction pattern of the crystallite.



References; (1) Biemann, K. et al., 1977. *Journal of Geophysical Research*, 82(28), pp.4641–4658. (2) Glavin, D.P. et al., 2013. *Journal of Geophysical Research: Planets*, 118(10), 1955–1973. (3) Steele, A. et al., 2012. *Science*, 337(6091), pp.212–215. (4) Stackelberg, M. v., 1949. *Feste Gashydrate. Die Naturwissenschaften*, 36(1), pp.327–333. (5) Dyadin, Y.A. et al., 1990. *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, 9(1), pp.37–49. (6) Seo, Y. & Lee, H., 2002. *The Journal of Physical Chemistry B*, 106(37), pp.9668–9673. (7) Chassefière, E., 2009. *Metastable Icarus*, 204(1), pp.137–144.