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LETTER

Nitrogen and carbon concentrations and isotopic compositions of the silica clathrate melanophlogite

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ABSTRACT

The concentrations and isotopic compositions of N and C were obtained for five melanophlogite samples, ideal formula $46SiO_2 \cdot 6(CO_2,N_2) \cdot 2(CH_4,N_2)$, from various localities in Italy and California, U.S.A. The melanophlogite crystals enclathrate 132 to 1674 ppm N presumed to be speciated as molecular N_2 and with $\delta^{15}N_{air}$ ranging from –6.1 to +5.7‰. The higher $\delta^{15}N$ values overlap those for organic/sedimentary N, the latter largely with values between 0 and +10‰. The samples also contain 1.2 to 2.9 wt% total C, with $\delta^{13}C_{VPDB}$ of –42.9 to –8.7‰, obtained from analyses of the bulk C in samples with probable varying proportions of CO_2 and CH_4 in the melanophlogite cages. Although the lower $\delta^{15}N$ values for the melanophlogites (–6.1 and –2.8‰) are near upper mantle values (–5 ± 2‰), the full range in N_2 $\delta^{15}N$ can be explained by equilibration with NH_4^+ in clay minerals bearing an organic-influenced N isotope signature, at temperatures of near 100 °C estimated for melanophlogite crystallization. The lower $\delta^{13}C$ values (as low as –42.9‰) are suggestive of equilibration with carbonaceous matter (poorly recrystallized organic material) at high cage CH_4:CO_2, perhaps representing lower oxygen fugacities. The growing number of reports of melanophlogite at terrestrial localities, and its occurrences in organic-rich settings, makes this clathrate mineral an intriguing candidate for preserving records of past surface or near-surface biogeochemical cycling on Earth and perhaps on Mars.

Keywords: Melanophlogite, nitrogen isotopes, carbon isotopes, microporous minerals, mass spectrometry, silica clathrate, biogeochemistry, Mars