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 46SiO2·6(CO2,N2)·2(CH4,N2), 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 N2 and with δ15N ranging from −6.1 to +5.7‰. The higher δ15N 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 δ13C VPDB of −42.9 to −8.7‰, obtained from analyses of the bulk C in samples with probable varying proportions of CO2 and CH4 in the melanophlogite cages. Although the lower δ15N values for the melanophlogites (−6.1 and −2.8‰) are near upper mantle values (−5 ± 2‰), the full range in δ15N can be explained by equilibration with NH3 in clay minerals bearing an organic-influenced N isotope signature, at temperatures of near 100 °C estimated for melanophlogite crystallization. The lower δ13C values (as low as −42.9‰) are suggestive of equilibration with carbonate bearing an organic-rich matter (poorly recrystallized organic material) at high cage CH4:CO2, 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

INTRODUCTION

Nitrogen-bearing minerals crystallizing in low-T surface or near-surface environments can potentially reveal information regarding the pathways for biogeochemically processed N into the solid inorganic Earth (Bebout et al. 2016). It is well known that various layer silicates, such as the clay minerals (e.g., illite), are important in this regard because they can incorporate NH3 into their crystal structures, in general substituting for K+. Other minerals could also be of interest in terms of N incorporation and, here, the microporous class of phases deserves attention. Melanophlogite, ideally 46SiO2·6(N2,CO2)·2(CH4,N2), a rare porosil or silica clathrate (Liebau 1988), is worthy of consideration because it can crystallize in near-surface hydrothermal environments and it can enclathrate N2 as well as CH4, CO2, and H2S molecules (Kamb 1965; Gies et al. 1982; Gies 1983; Kortus et al. 2000; Kolesov and Geiger 2003; Tribaudino et al. 2008; Momma 2014; Miyajima et al. 2016).

Melanophlogite shares some general similarities with the higher-T microporous minerals beryl and cordierite, but there are differences as well. In terms of similarity, all of these phases can contain various single, neutral molecular species in small pores in their crystal structures. The geochemical behavior of N2 in beryl and cordierite was recently investigated and the latter could serve as a sink for N in the shallow and middle continental crust (Bebout et al. 2016). Melanophlogite, unlike cordierite, occurs in lower-T, near-surface geologic environments. Also unlike beryl and cordierite, melanophlogite is hydrophobic and does not contain the polar H2O molecule in its structure.

A good deal of structural, crystal-chemical, and thermodynamic work has been conducted on melanophlogite, but relatively little study has been done investigating its geochemical properties, as revealed by its enclathrated molecules. In this brief contribution, we present, for the first time, N concentrations and isotope compositions for five different melanophlogite samples, taken from well-known localities in Italy and California, U.S.A. We discuss the degree to which this phase could serve as a host for storage of N (as N2). We also present bulk C concentrations and δ13C values of the same samples. These results hopefully will encourage further investigation of biogeochemical processes attending the crystallization of this unusual mineral phase and the extent to which the volatiles in its cages can provide records of these processes.

SAMPLES AND ANALYTICAL METHODS

Table 1 provides the sampling localities for the melanophlogites analyzed in this study. Nitrogen concentrations and isotope compositions were measured using carrier-gas methods described by Bebout et al. (2007). In our study, 9–17 mg of melanophlogite were loaded into quartz tubes with 1 g of CuO reagent and evacuated for 24 h before sealing. The tubes were heated at 1100 °C for 180 min, with the cooling history regulated to ensure separation of N as N2 and C as CO2 and H2O, respectively. The resulting N2 was purified cryogenically, then transferred into a Finnigan MAT 252 mass spectrometer via a Finnigan Gas Bench II. The analytical uncertainties for N concentrations are <5% and, for δ15N values (reported in standard δ convention, referenced to the isotopic composition of atmospheric N2 with isotopic ratio 15N/14N = 27.5; Mariotti 1994), uncertainty is ∼0.15‰ (1σ) for samples with >5 ppm.

Extraction of C from the same samples, after pretreatment with 1 N HCl to remove any carbonate, was undertaken similarly by heating the samples in sealed