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## Revision 1

# Nitrogen and Carbon Concentrations and Isotopic Compositions of the Silica Clathrate Melanophlogite

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## ABSTRACT

26       The concentrations and isotopic compositions of N and C were obtained for five  
27 melanophlogite samples, ideal formula  $46\text{SiO}_2 \cdot 6(\text{CO}_2, \text{N}_2) \cdot 2(\text{CH}_4, \text{N}_2)$ , from various localities in  
28 Italy and California, USA. The melanophlogite crystals enclathrate 132 to 1674 ppm N presumed  
29 to be speciated as molecular  $\text{N}_2$  and with  $\delta^{15}\text{N}_{\text{air}}$  ranging from -6.1 to +5.7‰. The higher  $\delta^{15}\text{N}$   
30 values overlap those for organic/sedimentary N, the latter largely with values between 0 and  
31 +10‰. The samples also contain 1.2 to 2.9 wt. % total C, with  $\delta^{13}\text{C}_{\text{VPDB}}$  of -42.9 to -8.7‰,  
32 obtained from analyses of the bulk C in samples with probable varying proportions of  $\text{CO}_2$  and  
33  $\text{CH}_4$  in the melanophlogite cages. Although the lower  $\delta^{15}\text{N}$  values for the melanophlogites (-6.1  
34 and -2.8‰) are near upper mantle values ( $-5 \pm 2\text{‰}$ ), the full range in  $\text{N}_2$   $\delta^{15}\text{N}$  can be explained  
35 by equilibration with  $\text{NH}_4^+$  in clay minerals bearing an organic-influenced N isotope signature, at  
36 temperatures of near  $100^\circ\text{C}$  estimated for melanophlogite crystallization. The lower  $\delta^{13}\text{C}$  values  
37 (as low as -42.9‰) are suggestive of equilibration with carbonaceous matter (poorly  
38 recrystallized organic material) at high cage  $\text{CH}_4:\text{CO}_2$ , perhaps representing lower oxygen  
39 fugacities. The growing number of reports of melanophlogite at terrestrial localities, and its  
40 occurrences in organic-rich settings, makes this clathrate mineral an intriguing candidate for  
41 preserving records of past surface or near-surface biogeochemical cycling on Earth and perhaps  
42 on Mars.

43 **Keywords:** melanophlogite, nitrogen isotopes, carbon isotopes, microporous minerals, mass  
44 spectrometry, silica clathrate, biogeochemistry

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## INTRODUCTION

48 Nitrogen-bearing minerals crystallizing in low-*T* surface or near-surface environments can  
49 potentially reveal information regarding the pathways for biogeochemically processed N into the  
50 solid inorganic Earth (Bebout et al., 2016). It is well known that various layer silicates, such as  
51 the clay minerals (e.g., illite), are important in this regard because they can incorporate  $\text{NH}_4^+$  into  
52 their crystal structures, in general substituting for  $\text{K}^+$  (Busigny and Bebout, 2013). Other  
53 minerals could also be of interest in terms of N incorporation and, here, the microporous class of  
54 phases deserves attention. Melanophlogite, ideally  $46\text{SiO}_2 \cdot 6(\text{N}_2, \text{CO}_2) \cdot 2(\text{CH}_4, \text{N}_2)$ , a rare porosil  
55 or silica clathrate (Liebau 1988), is worthy of consideration because it can crystallize in near-  
56 surface hydrothermal environments and it can enclathrate  $\text{N}_2$  as well as  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$   
57 molecules (Kamb, 1965; Gies et al., 1982; Gies, 1983; Kortus et al., 2000; Kolesov and Geiger,  
58 2003; Tribaudino et al., 2008; Momma et al., 2011; Momma, 2014; Miyajima et al., 2016).

59 Melanophlogite shares some general similarities with the higher-*T* microporous minerals  
60 beryl and cordierite, but there are differences as well. In terms of similarity, all of these phases  
61 can contain various single, neutral molecular species in small pores in their crystal structures.  
62 The geochemical behavior of  $\text{N}_2$  in beryl and cordierite was recently investigated and the latter  
63 could serve as a sink for N in the shallow and middle continental crust (Bebout et al., 2016).  
64 Melanophlogite, unlike cordierite, occurs in lower-*T*, near-surface geologic environments. Also  
65 unlike beryl and cordierite, melanophlogite is hydrophobic and does not contain the polar  $\text{H}_2\text{O}$   
66 molecule in its structure.

67 A good deal of structural, crystal-chemical and thermodynamic work has been conducted  
68 on melanophlogite, but relatively little study has been done investigating its geochemical  
69 properties, as revealed by its enclathrated molecules. In this brief contribution, we present, for

70 the first time, N concentrations and isotope compositions for five different melanophlogite  
71 samples, taken from well-known localities in Italy and California, USA. We discuss the degree  
72 to which this phase could serve as a host for storage of N (as N<sub>2</sub>). We also present bulk C  
73 concentrations and δ<sup>13</sup>C values of the same samples. These results hopefully will serve to  
74 encourage further investigation of biogeochemical processes attending the crystallization of this  
75 unusual mineral phase and the extent to which the volatiles in its cages can provide records of  
76 these processes.

## 77 **SAMPLES AND ANALYTICAL METHODS**

78 **Table 1** provides the sampling localities for the five melanophlogites analyzed in this  
79 study. Nitrogen concentrations and isotope compositions were measured using the methods  
80 described by Bebout et al. (2007). Liu et al. (1997) noted that the enclathrated molecules of  
81 melanophlogite can be released by heating above 600°C. In our study, 9 to 17 mg of  
82 melanophlogite were loaded into quartz tubes with 1 g of CuO<sub>x</sub> reagent and evacuated for 24  
83 hours before sealing. The tubes were heated at 1100°C for 180 minutes, with the cooling history  
84 carefully regulated to ensure speciation of N as N<sub>2</sub> and C and H as CO<sub>2</sub> and H<sub>2</sub>O, respectively.  
85 The resulting N<sub>2</sub> was purified in an all-metal extraction line, then transferred into a Finnigan  
86 MAT 252 mass spectrometer via a Finnigan Gas Bench II and a “homemade” U-trap interface,  
87 the latter into which small amounts of N<sub>2</sub> (typically 50-300 nanomoles) are transferred  
88 cryogenically before entrainment in a He stream. The analytical uncertainties for N  
89 concentrations are <5% and, for δ<sup>15</sup>N<sub>air</sub> values (reported in standard delta convention, referenced  
90 to the isotopic composition of atmospheric N<sub>2</sub> with isotopic ratio <sup>14</sup>N/<sup>15</sup>N = 272; Mariotti 1984),  
91 uncertainty is ~0.15‰ (1σ) for samples with > 5 ppm (see Bebout et al., 2007).

92 Extraction of C from the same samples, after pretreatment with 1N HCl to remove any  
93 carbonate, was undertaken similarly by heating the samples in sealed quartz tubes. In these  
94 extractions, larger amounts of melanophlogite (up to 116 mg) were required to allow  
95 measurement of the resulting CO<sub>2</sub> by dual-inlet mass spectrometry. This method allows a  
96 measurement of the  $\delta^{13}\text{C}$  (reported relative to VPDB) of the bulk C released during heating (i.e.,  
97 CH<sub>4</sub> and CO<sub>2</sub> in the cages is analyzed as bulk CO<sub>2</sub> gas). Uncertainties in C concentration are  
98 estimated at <5%, and uncertainties in  $\delta^{13}\text{C}$  (1 $\sigma$ ) are <0.1‰, for both estimates based on analyses  
99 of international and internal standards (e.g., the international NBS-24 graphite standard).

## 100 RESULTS AND DISCUSSION

101 The measured N and C concentrations and isotopic compositions of the melanophlogite  
102 samples are presented in **Table 1**. They contain between 132 and 1674 ppm of N with  $\delta^{15}\text{N}$   
103 ranging from -6.1 to +5.7‰. Several of the samples have  $\delta^{15}\text{N}$  somewhat lower than the range of  
104 ~0 to +10‰ for organic/sedimentary materials. Bulk C concentrations in the five  
105 melanophlogites range from 1.24 to 2.88 wt. %, far higher than the N concentrations in the same  
106 samples (i.e., C/N ratios range from 8 to 187; **Table 1**). The C concentrations for melanophlogite  
107 from Racalmuto, Italy, and Mt. Hamilton, California, are similar to those obtained presented by  
108 Beard et al. (2013) for melanophlogite from the same localities.  $\delta^{13}\text{C}$  ranges from -42.9 to -8.7‰  
109 and the three melanophlogites with the lowest  $\delta^{13}\text{C}$  (-42.0 to -32.8‰) also have the lowest  $\delta^{15}\text{N}$   
110 values (-6.1 to -2.5‰).

### 111 Geological occurrence and stability of melanophlogite

112 Melanophlogite was first described by von Lasaulx (1876) as occurring in the well-known  
113 Sicilian sedimentary S deposits (e.g., Giona Mine, Milena, Caltanissetta Province, Sicily; see

114 Dessau et al., 1962). It has since been found at a number of different localities worldwide (see  
115 Beard et al., 2013; Houseley, 2013). In several cases, it occurs in near-surface, volcanic-  
116 sedimentary paleohydrothermal systems in fractures or druse cavities as euhedral crystals (e.g.,  
117 Mt. Hamilton, CA; Chvaletice, Bohemia; Varano Marchesi, Parma, Italy). Reed (1937) reported  
118 occurrences of melanophlogite in amygdules in Columbia River volcanic rocks (USA). Skinner  
119 and Appleman (1963) estimated formation temperatures of less than 112°C as indicated by  
120 melanophlogites “encrusting sulfur ..... crystals”. In the laboratory, melanophlogite crystals can  
121 be synthesized at 170°C and approximately 150 bar (Gies et al., 1982). In the case of the Sicilian  
122 S deposits, Skinner and Appleman (1963), citing Friedel (1890), write “the sulfur mines were  
123 dripping with bitumen, and it is possible that the melanophlogite may actually have been  
124 deposited from the bitumen.” Other geologic occurrences have been recently reported, for  
125 example, melanophlogite at a seafloor vent site in the Cascadia accretionary prism (Kohler et al.,  
126 1999), in marine siliceous sediments (Adorni and Tateo, 2007), and in a Miocene methane seep-  
127 deposit exposed on land near Joetsu, Japan (Miyajima et al., 2016). The growing number of  
128 occurrences in near-surface, relatively low-*T* environments indicates that melanophlogite is  
129 likely to be more abundant than previously recognized.

130 The thermodynamic stability and crystallization process of melanophlogite were discussed  
131 in Geiger et al. (2008). Melanophlogite often occurs with other SiO<sub>2</sub> minerals such as cristobalite  
132 and chalcedony or opal (Žák, 1972; Cooper and Dunning, 1972; Dunning and Cooper, 2002;  
133 Tribaudino et al. 2008). At Racalmuto, Italy, for example, melanophlogite occurs with opal and  
134 quartz and is often nucleated around these phases (Skinner and Appleman 1963).  
135 Melanophlogite’s thermodynamic properties (Navrotsky et al., 2003; Geiger et al., 2008) and its  
136 field occurrence are consistent with one another and indicate metastable crystallization (Geiger et

137 al., 2008). Gies et al. (1982) noted that melanophlogite can transform to quartz upon grinding.  
138 However, melanophlogite may crystallize in nature more often than realized, as it is not easily  
139 recognized and it is readily pseudomorphed by other SiO<sub>2</sub> phases (e.g., cristobalite; Beard et al.,  
140 2013, also see Housely, 2013 for description of newly reported melanophlogite occurrences in  
141 southern California, USA).

#### 142 **Crystallization and enclathration of nitrogen and carbon in melanophlogite**

143 Whether or not melanophlogite is metastable, it enclathrates various simple molecules of  
144 interest to those investigating surface/near-surface biogeochemical cycling. Diffraction and  
145 vibrational spectroscopic study (Gies 1983; Kortus et al., 2000; Kolesov and Geiger, 2003), as  
146 well as simple mass spectrometry measurements (Gies et al. 1982), show that, either alone  
147 (Varano Marchesi, Parma, Italy - Tribaudino et al., 2008) or in combination, CH<sub>4</sub>, N<sub>2</sub>, CO<sub>2</sub>, and  
148 H<sub>2</sub>S molecules can be present. Melanophlogite has no essential “OH” (cf. Beard et al., 2013) or  
149 H<sub>2</sub>O molecules to the best of our knowledge (i.e., it is hydrophobic). It is clear, though, that CH<sub>4</sub>,  
150 N<sub>2</sub>, CO<sub>2</sub> (Gies et al. 1982; Kortus et al., 2000; Kolesov and Geiger, 2003), and H<sub>2</sub>S (Tribaudino  
151 et al., 2008) molecules serve as structure-directing-agents and are a prerequisite for  
152 crystallization as shown by Gies et al. (1982; 1998). There are two distinct micropores or cages  
153 in the structure, namely the smaller [5<sup>12</sup>] and larger [5<sup>12</sup>6<sup>2</sup>] cages (**Fig. 1**). Where precisely N<sub>2</sub> is  
154 located is uncertain, with Gies (1983) suggesting both cages with N<sub>2</sub> predominantly in [5<sup>12</sup>6<sup>2</sup>],  
155 while Gies et al. (1998) state “almost 100 % occupancy in the smaller...[5<sup>12</sup>] cages.” Single-  
156 crystal Raman measurements at room temperature and 4 K show only one narrow N<sub>2</sub> symmetric-  
157 stretching peak at 2321 cm<sup>-1</sup>, indicating that the molecule is likely enclathrated in just one cage  
158 (Kolesov and Geiger, 2003).

159           The relatively high concentrations of N measured here confirm the results of an early mass  
160 spectrometry study (Gies et al. 1982). However, for the melanophlogite sample from Mt.  
161 Hamilton, CA, Gies (1983) calculated molecular CO<sub>2</sub>:N<sub>2</sub>:CH<sub>4</sub> ratios of 1:3.6:1.8, whereas in the  
162 Mt. Hamilton melanophlogite we analyzed, concentrations of bulk C exceeded those for N (see  
163 **Table 1**). There can be, though, strong variations in molecular concentrations even in the same  
164 crystal (Gies et al. 1982). Variations in the N contents and N/C ratios among the five samples  
165 point to diverse fluid compositions in the paleohydrothermal environment from which  
166 melanophlogites crystallized. The Raman spectroscopy performed by Tribaudino et al. (2008)  
167 indicated varying proportions of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in melanophlogites from Mt. Hamilton,  
168 Livorno, and Racalmuto, and among melanophlogites from specific localities, leading those  
169 authors to suggest that concentrations of these volatiles vary considerably at any individual  
170 locality. Two simple geochemical scenarios to explain the measured N<sub>2</sub> isotopic compositions in  
171 melanophlogite are: i) melanophlogite incorporates N<sub>2</sub> of the same isotopic composition as the  
172 N<sub>2</sub> in the fluid from which it crystallizes, or ii) <sup>14</sup>N or <sup>15</sup>N is preferentially fractionated into the  
173 cages during crystallization. For this second scenario, the negative δ<sup>15</sup>N values could thus be  
174 interpreted as indicating an enrichment of <sup>14</sup>N relative to a coexisting fluid with a more positive  
175 δ<sup>15</sup>N value. The two scenarios would also apply to the incorporation of CO<sub>2</sub> and CH<sub>4</sub> into the  
176 melanophlogite cages, but instead involving <sup>13</sup>C and <sup>12</sup>C. Unfortunately, the isotopic  
177 compositions of the fluids present during melanophlogite crystallization could not be determined  
178 making it impossible to evaluate the two possibilities. However the vibrational IR and Raman  
179 spectra of the melanophlogite from Mt. Hamilton (see **Table 1**) provide information regarding  
180 the energetic state of the enclathrated molecules (Kolesov and Geiger 2003). The symmetric  
181 stretching band of N<sub>2</sub> in melanophlogite is located at 2321 cm<sup>-1</sup> compared to 2330.7 cm<sup>-1</sup> for the



182 case of a free gaseous N<sub>2</sub> molecule. The relatively small difference in the two energies indicates  
183 a weak interaction of the N<sub>2</sub> molecules with the SiO<sub>2</sub> framework of melanophlogite. Thus, there  
184 should be no great driving force for strong N isotope fractionation between fluid and crystals  
185 during the incorporation of the N<sub>2</sub> (i.e., the δ<sup>15</sup>N of the N<sub>2</sub> in the melanophlogite should be the  
186 same as that of the N<sub>2</sub> in the fluids during melanophlogite crystallization).

### 187 **Interpretation of the nitrogen and carbon isotope compositions of the melanophlogites**

188 **Figure 2** demonstrates fluid-rock C and N isotope fractionation that could have exerted  
189 control over the isotopic compositions of the melanophlogites, applying a Rayleigh fractionation  
190 model (for a temperature of 100°C; sources of the fractionation factors are given in the figure  
191 caption). In these calculations, the C and N in the source (hydrothermally altering sedimentary  
192 rocks) are in carbonaceous matter (poorly recrystallized organic matter, here modeled as  
193 graphite) and as NH<sub>4</sub><sup>+</sup> in clay minerals, respectively. During the heating, fractionated C and N  
194 are lost from these sedimentary rocks, resulting in shift in the isotopic compositions of the  
195 residual sedimentary rock reservoirs and later-released C and N fluid species. In **Fig. 2A**, the  
196 dashed lines indicate the evolution of the fluid N<sub>2</sub> lost from a sedimentary rock with initial δ<sup>15</sup>N  
197 of 0‰ and +2‰. The N<sub>2</sub> in fluids released from rocks with this range in initial compositions  
198 would be expected to have δ<sup>15</sup>N values between the two dashed lines. Although the lower  
199 melanophlogite δ<sup>15</sup>N values are near upper mantle values (-5 ± 2‰; Cartigny and Marty, 2013;  
200 see the range indicated on **Fig. 2A**), the full range of values (about -6 to +6‰) can more  
201 plausibly be explained by equilibration of N<sub>2</sub> with NH<sub>4</sub><sup>+</sup> in clay minerals bearing an organic N  
202 isotope signature, at temperatures of near 100°C estimated for melanophlogite crystallization.

203 **Figure 2B** similarly demonstrates the likely evolution in fluid C isotope compositions, showing  
204 the evolution of a pure CO<sub>2</sub> and a pure CH<sub>4</sub> fluid emanating from the sedimentary source, as a

205 function of the fraction of the initial C lost from the rocks (see the dashed blue and red lines,  
206 respectively). Stabilization of both CO<sub>2</sub> and CH<sub>4</sub> in the fluids (see the studies of mixed CO<sub>2</sub>-  
207 CH<sub>4</sub>-N<sub>2</sub> fluid inclusions by van der Kerkhof, 1990; Seitz et al., 1994) would result in evolution  
208 of fluids (and rock residues) with δ<sup>13</sup>C intermediate between these two end-members. The lower  
209 melanophlogite δ<sup>13</sup>C values (as low as -42.9‰) could reflect high cage CH<sub>4</sub>:CO<sub>2</sub>, perhaps  
210 representing equilibration with the carbonaceous matter at lower oxygen fugacities. Relatively  
211 reducing conditions during melanophlogite crystallization also are indicated by occurrences of  
212 melanophlogite with elemental S and bitumen at the classic Sicilian localities.

### 213 **IMPLICATIONS AND OUTLOOK FOR FUTURE RESEARCH**

214 Melanophlogite can contain appreciable N with concentrations between 132 and 1674 ppm,  
215 and C with concentrations of up to 2.9 wt. %, the latter in varying proportions of CO<sub>2</sub> and CH<sub>4</sub>.  
216 The isotopic compositions of this N and C appear consistent with release by heating of a  
217 sedimentary source and the wide range of δ<sup>13</sup>C values could in part reflect differing CO<sub>2</sub>:CH<sub>4</sub>  
218 possibly related to the oxygen fugacity of the environment during fluid loss. This reconnaissance  
219 study points to the need for more detailed investigation of the mechanisms behind N<sub>2</sub>  
220 incorporation into melanophlogite and whether the measured isotopic compositions directly  
221 reflect biogeochemical processes operative during its crystallization. Future research should  
222 focus on more thorough study of the individual geological settings in which melanophlogite  
223 formed, in order to identify sources and possible biogeochemical pathways for N and C. Here,  
224 where possible, direct study of the geochemistry of the fluids involved would be extremely  
225 useful (i.e., in modern settings in which melanophlogite is being formed).

226 Finally, it has been speculated that Mars' surface could contain abundant zeolite and  
227 amorphous, perhaps opaline silica-rich phases (Milliken et al., 2008; Skok et al., 2010). This

228 raises the question regarding the possible occurrence of melanophlogite. If it were to occur on  
229 Mars, it would very useful for understanding surface/near-surface geologic processes involving  
230 the storage of possible organically derived CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. Minerals, such as the silica  
231 clathrates, zeolites, in addition to clays, if present on Mars' surface, perhaps, in part, as alteration  
232 products of volcanic rocks and as cements in clastic rocks, could contain NH<sub>4</sub><sup>+</sup> and/or N<sub>2</sub>. The  
233 isotopic compositions of these two N species could provide information on any possible  
234 (bio)geochemical activity on the planet.

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## FIGURE CAPTIONS

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**Figure 1.** (a) Polyhedral structure model of the cubic high-T modification of melanophlogite. The dark polyhedra are the smaller  $[5^{12}]$  cages and the green the larger  $[5^{12}6^2]$  cages. The spheres represent enclathrated molecular species. (b) Melanophlogite from Mt. Hamilton (horizontal dimension is 2 cm; photograph from <http://minerals.caltech.edu>; similar to sample “Mt. Hamilton”). (c) Botryoidal melanophlogite from Cianciana, Agrigento, Italy (horizontal dimension is 10 cm; sample 40820; photograph courtesy of J. Newman, American Museum of Natural History, NY). See **Figure S1** for photographs of other samples analyzed in this study.

**Figure 2.** Calculated Rayleigh fractionation for evolution of fluid-mineral N and C isotope evolution (see Svensen et al., 2008, for a description of the application of the Rayleigh model in a similar scenario). (a) Calculation for loss of  $N_2$  from  $NH_4^+$  (the latter presumed to be in clay minerals in the sedimentary rock source). As isotopically light N is lost as  $N_2$  from the sedimentary  $NH_4^+$  reservoir, the sedimentary residue shifts toward higher  $\delta^{15}N$  (solid lines for initial  $\delta^{15}N$  of 0‰ and 2‰), thereafter releasing  $N_2$  with similarly increased  $\delta^{15}N$ . The range of mantle  $\delta^{15}N$  is from Cartigny and Marty (2013). (b) Calculated loss of C as either  $CO_2$  or  $CH_4$  from a sedimentary reservoir containing C in “graphite” (poorly recrystallized organic material). Loss of the C as  $CO_2$  or  $CH_4$  results in opposite trends in  $\delta^{13}C$ , with loss as  $CO_2$  resulting in shift in the residue (and later-released fluid  $CO_2$ ) toward lower  $\delta^{13}C$ , and loss as  $CH_4$  resulting in shift in both the “graphite” and later released  $CH_4$  toward higher  $\delta^{13}C$ . Release of C in mixed  $CO_2$ - $CH_4$  fluids would result in fluid and “rock” evolution intermediate to the two shown paths shown in this figure. The fractionation factor for the N isotope calculations in (A) was derived from polynomial constants in Petts et al. (2015; this fractionation factor is similar to that calculated for 100°C by Hanschmann (1981; see the compilation in Busigny and Bebout, 2013). For the calculations of C isotope compositions in (B), the fractionation factors were from Horita (2001;  $CO_2$ - $CH_4$ ) and Ohmoto and Rye (1979; graphite- $CO_2$ ). The “F” (x-axis) in (A) and (B) is the fraction of the initial N or C remaining in the “rock.”

**Table 1.** Nitrogen and carbon concentrations and isotopic compositions of the melanophlogite samples

<b>Sample</b>	<b>Country</b>	<b>Province/State</b>	<b>County</b>	<b>City</b>	<b>N (ppm)</b>	<b><math>\delta^{15}\text{N}_{\text{air}}</math></b>	<b>C (wt.%)</b>	<b><math>\delta^{13}\text{C}_{\text{VPDB}}</math></b>	<b>C/N</b>
40820	Italy	Sicily	Agrigento	Cianciana	641	5.7	2.76	-8.7	43
4361	Italy	Sicily	Agrigento	Racalmuto	1674	-6.1	1.34	-32.8	8
4367	Italy	Tuscany	Livorno	Livorno	132	-2.8	2.11	-34.3	160
81120	Italy	Sicily	Agrigento	Racalmuto	154	-1.5	2.88	-42.9	187
Mt. Hamilton	USA	California	Santa Clara	---	436	0.2	1.24	-29.2	28



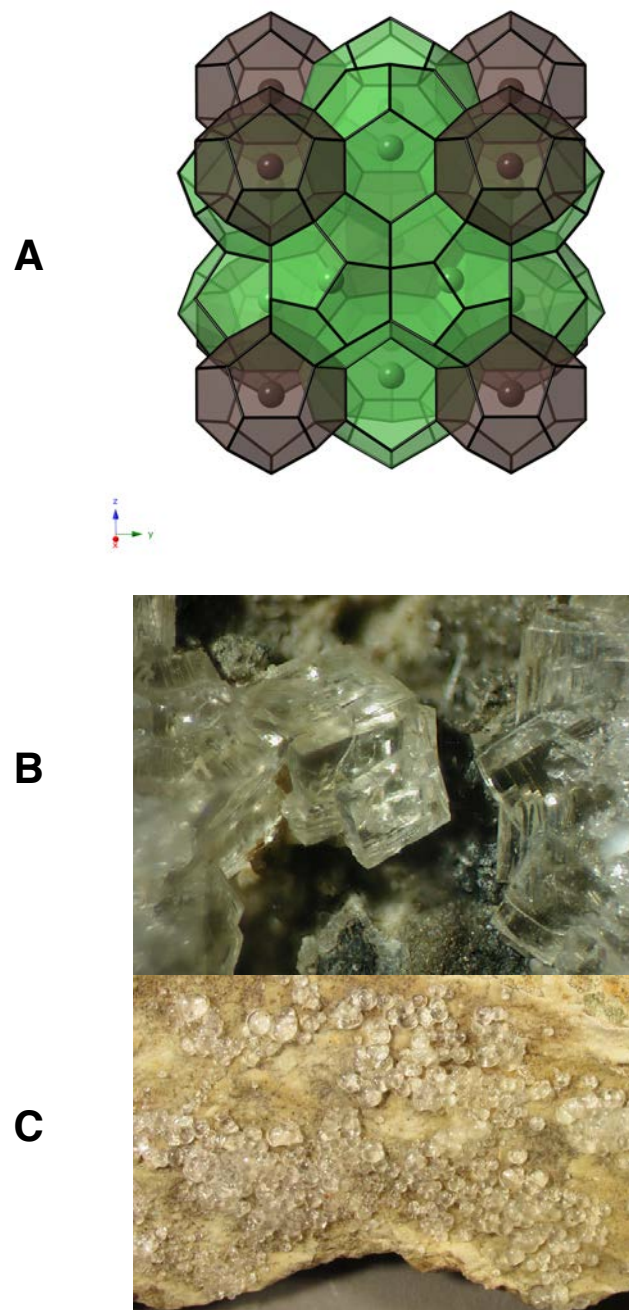


Fig. 1

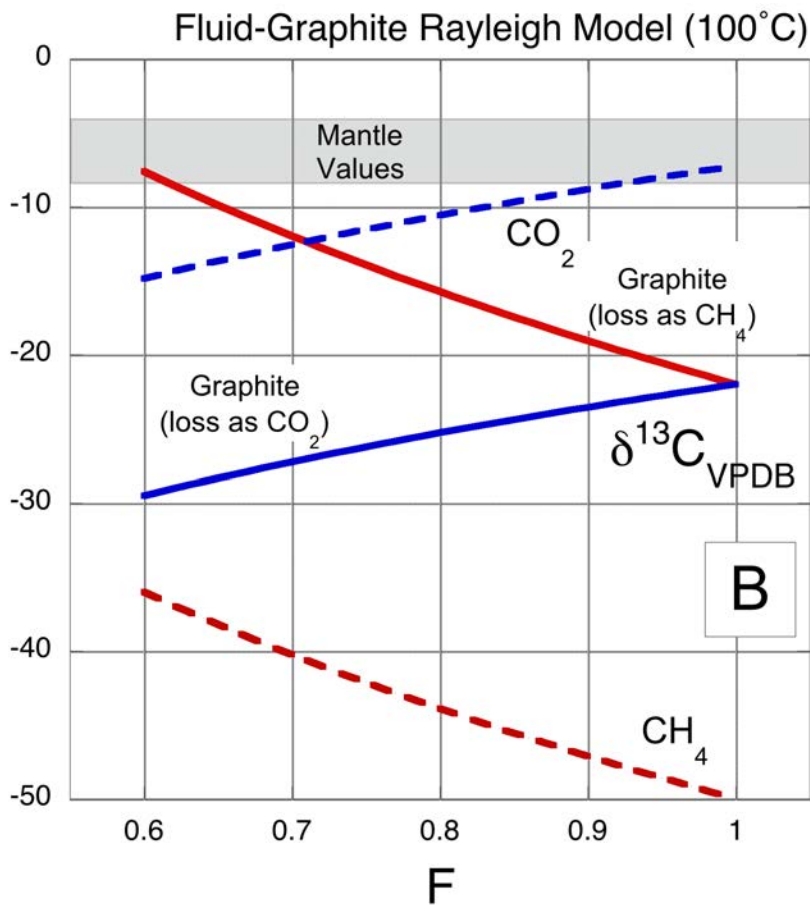
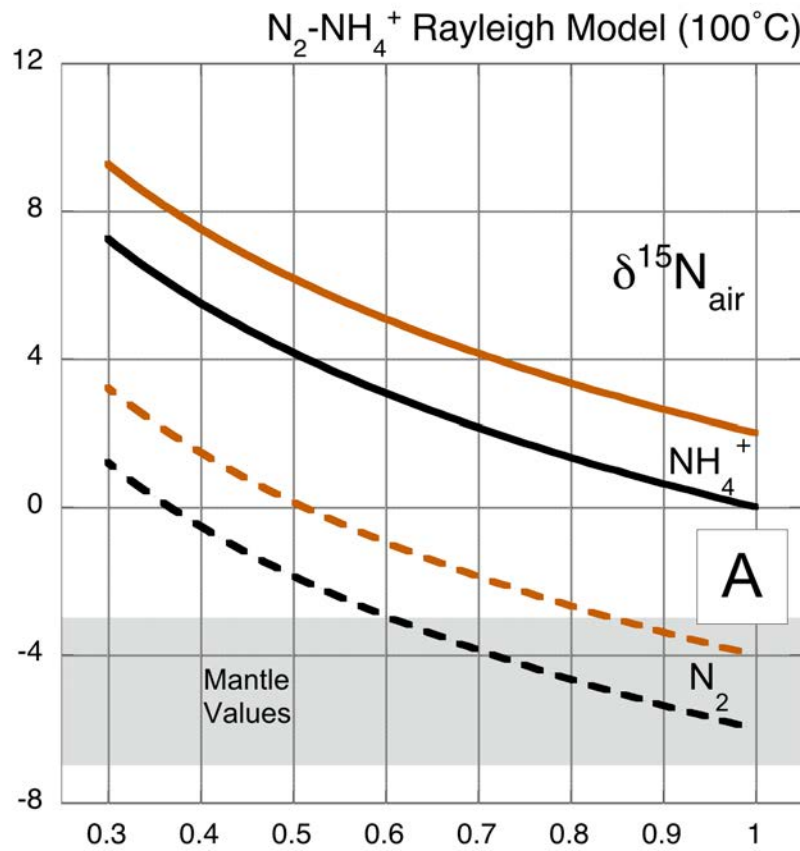


Fig. 2