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LETTER

Heat capacity and entropy of melanophlogite: Molecule-containing porosils in nature

CHARLES A. GEIGER,[1,*] EDGAR DACHS,[2] AND MARIKO NAGASHIMA[1]

[1]Institut für Geowissenschaften, Abteilung Mineralogie, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
[2]Fachbereich Materialforschung und Physik, Abteilung Mineralogie, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

ABSTRACT

The heat capacities of two different molecule-containing melanophlogites of approximate composition $46SiO_2 \cdot 1.80CH_4 \cdot 3.54N_2 \cdot 1.02CO_2$ from Mt. Hamilton, California, and $46SiO_2 \cdot 3.59CH_4 \cdot 3.10N_2 \cdot 1.31CO_2$ from Racalmuto, Sicily, along with a heat-treated (molecule-free) sample of composition SiO_2, were studied between 5 and 300 K using heat-pulse microcalorimetry. The molecule-free sample was obtained by heating natural Racalmuto crystals at 1173 K for 24 h. The standard third-law entropy of the molecule-free sample is $S° = 2216.3 \pm 6.6$ J/(mol·K) for $46SiO_2$ and the natural Mt. Hamilton and Racalmuto samples give $S° = 2805.7 \pm 8.4$ J/(mol·K) and $S° = 2956.8 \pm 8.9$ J/(mol·K), respectively. The entropy and Gibbs free energy for molecule-free melanophlogite relative to quartz at 298 K are $\Delta S_{trans} = 6.7$ J/(mol·K) and $\Delta G_{trans} = 7.5$ kJ/mol, respectively and, thus, it does not have a thermodynamic field of stability in the SiO_2 system. The difference in C_P values between molecule-containing and molecule-free melanophlogite is characterized by an increase in C_P from 0 to ~70 K, and it then reaches a roughly constant value at 70 K < T < 250 K. The ΔS^{rxn} at 298 K for $46SiO_2$(melan.) + xCH_4(gas) + yCO_2(gas) + zN_2(gas) = $46SiO_2 \cdot (xCH_4)^{12} \cdot (yCO_2, zN_2)^{14}$ is estimated to be about –642 and –802 J/(mol·K) for the Mt. Hamilton and Racalmuto samples, respectively. The thermodynamic data, as well as published results on the occurrence of natural molecule-containing samples suggest that melanophlogite crystallizes metastabily. The occurrence of melanophlogite and the lack of other porosils in nature are probably due to the essential role of molecular structure-directing agents. For melanophlogite they can be CO_2, N_2, and CH_4, whereas the crystallization of other porosils requires more chemically and structurally complex molecules that are not naturally abundant.

Keywords: Melanophlogite, heat capacity, entropy, clathrasils, microporous minerals, clathrate