K-cymrite as Redox Insensitive Transporter of Nitrogen in the Mantle

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The current flux of nitrogen into the mantle in subduction zones is about three times its amount outgassing at mid-ocean ridges, arc and intraplate volcanoes, i.e., some efficient nitrogen hosts and carriers should exist in slabs. The $K^+ \rightarrow (NH_4^+)$ substitution in silicate minerals is possible only within limited redox-favorable parts of slabs. Whether nitrogen can be transported and immobilized in the mantle as part of solids by some redox-independent mechanisms? The experimental study of the muscovite-NH$_3$-N$_2$-H$_2$O and eclogite+muscovite-NH$_3$-N$_2$-H$_2$O systems at 6.3-7.8 GPa and 1000 to 1200°C shows that NH$_3$- and N$_2$-rich K-cymrite can be stable in metapelite and act as a redox insensitive carrier of nitrogen to mantle depths >200 km in downgoing slabs. This ability is related to its unique clathrate structure that can accommodate three species of nitrogen: N$_2$ and NH$_3$ molecules in cages and (NH$_4^+$) substituting for K$^+$, while imprisoned N$_2$ and NH$_3$ were first discovered in cages of ultra-high pressure minerals. The storage capacity K-cymrite with respect to nitrogen increases from 2.9 to 6.3 wt.% with increase of fO$_2$ from ~IW to ~NNO, at the N$_2$/($NH_3$+N$_2$) ratio in fluid from 0.1 to 0.9. Comparison of equilibrated muscovite and K-cymrite synthesized at 7.8 GPa, 1070°C, and fO$_2$ ~IW demonstrates that the clathrate mechanism of nitrogen entrapment by aluminosilicates (in the form of N$_2$ and NH$_3$ molecules) is much more efficient than the K$^+ \rightarrow (NH_4^+)$ substitution even in strongly reduced conditions. The presence of an N-bearing fluid in the studied systems stabilizes the K-cymrite structure. Muscovite does not convert to K-cymrite in the absence of NH$_3$-N$_2$-bearing fluid within 7.8 GPa and 1070-1120°C. Our estimates of normalized volume per non-hydrogen atom show that N$_2$-bearing cymrite is the densest in the series of K-cymrite with cages filled to different degrees: $K\text{Cym}_{NH_3} > K\text{Cym}_{H_2O} > K\text{Cym}_{N_2}$ and is thus the most stable among cymrite-type compounds under high pressure.

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