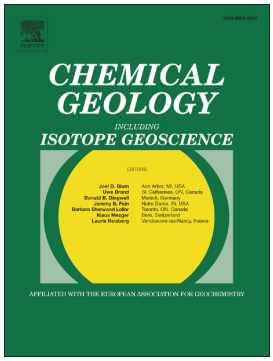

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The limitations of hibonite as a single-mineral oxybarometer for early solar system processes

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Abstract

The relationships between the composition of hibonite with the general formula $CaAl_{12-2x-y}Mg_xTi^{4+}{}_xTi^{3+}{}_yO_{19}$, the oxidation state of Ti ($Ti^{3+}/\Sigma Ti$, where $\Sigma Ti = Ti^{3+} + Ti^{4+}$), and oxygen fugacity ($fO_2$) were investigated experimentally. It was found that hibonite can be synthesised with a range of $Ti^{3+}/\Sigma Ti$ values at constant fO_2 and with a constant $Ti^{3+}/\Sigma Ti$ value for a range of fO_2s. It was also found that if hibonite with the formula $CaAl_{12-y}Ti^{3+}{}_yO_{19}$ ($Ti^{3+}/\Sigma Ti = 1$) is equilibrated with a melt of CAI composition at fO_2s below the iron-wüstite buffer then the resulting hibonite contained Mg, with Mg per formula unit (pfu) ~ 0.8 Ti pfu, and $Ti^{3+}/\Sigma Ti$ ~ 0.2, irrespective of the fO_2. These results suggest that the availability of Mg, rather than fO_2, is the key factor that determines $Ti^{3+}/\Sigma Ti$ of hibonite. The structures of synthetic samples of hibonite with the general formula $CaAl_{12-2x}Mg_xTi^{4+}{}_xO_{19}$, where $0 \leq X < 1$, were determined by Rietveld refinement of X-ray powder diffraction data. The predominant site occupied by Ti^{4+}