

## Additional observations on the ferric ion ( $\text{Fe}^{3+}$ ) content of melt-grown fayalite ( $\text{Fe}_2\text{SiO}_4$ )<sup>1</sup>

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Finch *et al.* (1980) reported the Czochralski (melt) growth of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and recorded solution colorimetric analyses for  $\text{Fe}^{3+}$  in representative crystals. The best material, grown at an oxygen fugacity of  $10^{-12}$  bar, was quoted to contain 0.27 to 0.51 wt.%  $\text{Fe}^{3+}$ . The dark-colored samples (not attracted to a small magnet) had been dissolved in HCl under argon, and the solution complexed with thiocyanate ion at 295 K. The results appeared consistent with literature data, and the dark color of the crystals was thought to be due to  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  transitions (Wickersheim and Lefever, 1962). In addition, the  $\text{Fe}^{3+}$  analyses were supported by the presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) inclusions in regions grown under non-optimal conditions.

Subsequent heat capacity measurements on this material (Robie *et al.*, 1982) did not reveal  $\text{Fe}^{3+}$  (no magnetite "bump" at 110–120 K), but the 1.0 wt.% lower detection limit did not preclude  $\text{Fe}^{3+}$  at the 0.27 to 0.51 wt.% level suggested by the colorimetric analyses. Definitive conflicting results came from electron paramagnetic resonance (EPR) studies performed at 77 K, which indicated an apparent absence of  $\text{Fe}^{3+}$ , *i.e.*, <0.001 wt.% (10 ppm). Resolution of the problem by magnetic circular dichroism measurements was not feasible, due to the biaxial optic nature of the orthorhombic fayalite (personal communication, B. Bliat, 1980, Laboratoire d'Optique Physique, Paris).

We have received the results of a high-sensitivity Mössbauer study (personal communication, D. Virgo, 1980, Geophysical Laboratory) which offered a threshold of  $\text{Fe}^{3+}$  detection at approximately 0.27 wt.% (2700 ppm). This Mössbauer study was conducted on a fayalite crystal whose single-phase character and freedom from magnetite inclusions had been verified by petrographic methods. The analysis did not reveal  $\text{Fe}^{3+}$  to be present, confirming that fayalite grown at an  $f(\text{O}_2)$  of  $10^{-12}$  bar contains less than 0.27 wt.%  $\text{Fe}^{3+}$  at 77 K (and probably considerably less than this based on the EPR results).

The high solution colorimetry results might be due to a reversible increase (in air) of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio between 77 and 295 K, but more likely are due to the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during analysis, in spite of precautions taken to prevent this. Our conclusions suggest a high bias of solution colorimetry results at low  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios. The dark color of fayalite may be due to metal-metal electron transfer bands around 5000 Å, but additional work would be necessary to confirm this.

### References

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