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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(Si–O) = 0.005 Å
R factor = 0.041
wR factor = 0.089
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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This is the first structural refinement of the mineral wilkinsonite, $Na_2Fe_4^{2+}Fe_2^{3+}Si_6O_{20}$. Wilkinsonite is a member of the aenigmatite group and consists of bands of Fe octahedra connected to eight-coordinated Na polyhedra forming sheets parallel to (011), which are interconnected by chains of $[Si_6O_{18}]_\infty$ and Fe octahedra. The site occupancies of the different valence states of Fe have been determined from bond distances and bond valence

Comment

Wilkinsonite belongs to the aenigmatite group of minerals with the general formula $A_2B_6T_6O_{20}$, where the A cations are observed as Na and Ca, B cations as Fe^{2+}, Fe^{3+}, Mg, Al, Cr, Ti and Sb^{5+}, and T cations as Si, Al, B and Be. Wilkinsonite is the Ti-free end member of the Na-aenigmatite mineral series, with aenigmatite, $Na_2Fe_5^{2+}TiSi_6O_{20}$ (Kelsey & McKie, 1964), at the other end of the limited solid solution series. Wilkinsonite was first synthesized by Ernst (1962) and later discovered by Duggan (1990) in a silica-undersaturated trachyte from Warrumbungle Volcano, Australia. This is the only known location for wilkinsonite, which occurs there as grains < 50 µm in diameter, hindering previous attempts at determining the crystal structure from X-ray diffraction data.

Wilkinsonite (Fig. 1) is isostructural with aenigmatite and contains bands of Fe octahedra that are linked to eight-coordinated Na polyhedra, forming sheets in the (011) plane (Fig. 2). The Fe and Na polyhedral sheets are connected by $[Si_6O_{18}]_\infty$ chains parallel to [100] and connecting Fe octahedra (Fig. 3).

The most significant structural difference between aenigmatite and wilkinsonite is the location of the Fe^{3+} cations in the structure of wilkinsonite. Refinement of the site occu-

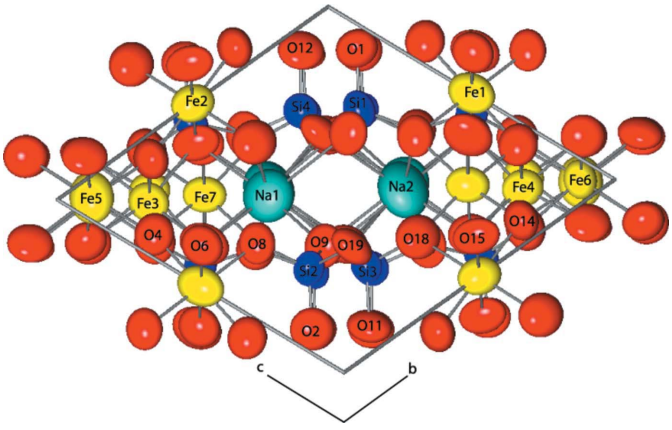

Figure 1
The crystal structure of wilkinsonite, viewed down the [100] direction. Displacement ellipsoids are drawn at the 99.99999% probability level.

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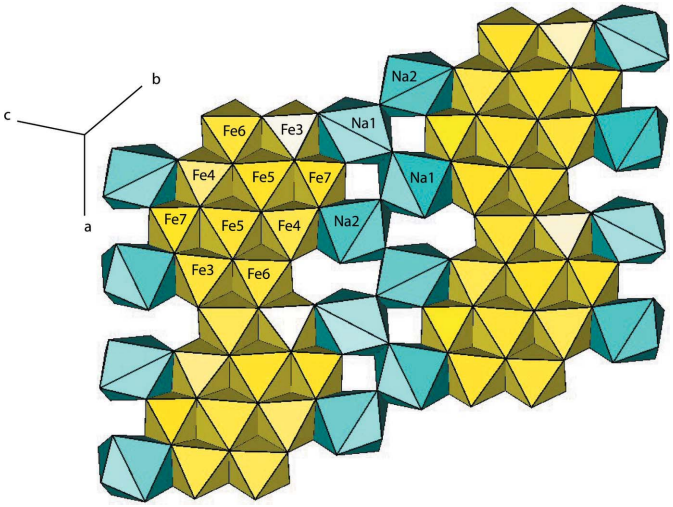

Figure 2
Bands of Fe octahedra connected by Na polyhedra in the (011) plane.

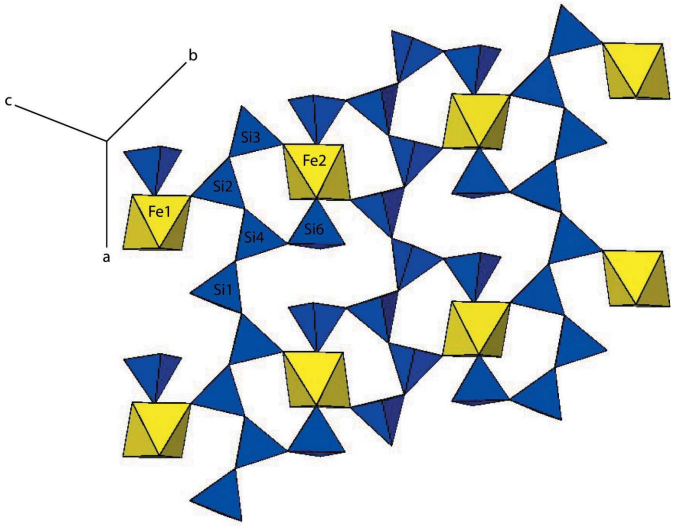

Figure 3
The (011) projection of the second layer, showing the $[Si_6O_{18}]_\infty$ chains along [100] and the connecting Fe octahedra.

pancies in aenigmatite indicates that, to some degree, Ti occupies all octahedral sites with the exception of the M6 site, and the small amount of Fe^{3+} is contained in a tetrahedral site (Cannillo *et al.*, 1971). Of the seven octahedral sites in aenigmatite, the highest concentration of Ti is found in the octahedra with an average bond length of 1.98 Å, compared with the larger octahedral sites where the average bond lengths range between 2.10 and 2.17 Å. In wilkinsonite, the Fe^{3+} cations are located in the Fe1, Fe2 and Fe7 sites, where the average bond length varies between 2.033 and 2.053 Å, compared with the other larger Fe^{2+} octahedral sites, Fe3, Fe4, Fe5 and Fe6, where the average bond length varies between 2.129 and 2.157 Å. Additionally, the Fe site valences and Fe^{3+} site-occupancy percentages have been determined using the bond-valence analysis of Brown & Altermatt (1985) and Brown (2002), giving site valences and Fe^{3+} percentages of, respectively: Fe1 2.87 and 84%, Fe2 2.75 and 70%, Fe3 2.06 and 7%, Fe4 2.09 and 11%, Fe5 1.92 and −9%, Fe6 1.99 and −1%, and Fe7 2.85 and 82%. This suggests that there are preferential Fe^{2+} and Fe^{3+} octahedral sites in wilkinsonite compared with the variable Fe^{2+} and Ti^{4+} octahedral sites in aenigmatite and this may affect the coupled substitution, $Fe^{2+} + Ti \rightarrow 2Fe^{3+}$ (Duggan, 1990), that defines the solid solution between the two minerals.

Experimental

The wilkinsonite crystal in this study is from the Warrumbungle Volcano, central New South Wales, Australia, and is part of the RRUFF project (deposition No. R060922; http://rruff.info). The chemical composition, $Na_{2.00}(Fe^{2+}_{3.840}Mn_{0.16})_4(Fe^{3+}_{1.885}Cr_{0.06}Ti_{0.055})_2(Si_{5.945}Al_{0.055})_6O_{20}$, was determined with a CAMECA SX50 electron microprobe (http://rruff.info). Although the microprobe analysis indicated small amounts of Mn, Cr, Ti and Al, structural refinements with partially occupied sites did not produce any significant differences in the *R* factors, bond distances or bond angles. Thus, the final refinement was completed with the chemical composition of an ideal wilkinsonite crystal.

Crystal data

$Fe_6Na_2O_{20}Si_6$
M_r = 869.62
Triclinic, $P\overline{1}$
a = 10.3355 (5) Å
b = 10.7847 (4) Å
c = 8.9142 (4) Å
α = 105.048 (3)°
β = 96.461 (3)°
γ = 125.302 (2)°
V = 738.37 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 6.42 mm^{-1}
T = 296 (2) K
0.05 × 0.05 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2005)
T_{min} = 0.733, T_{max} = 0.774
16331 measured reflections
4312 independent reflections
2812 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.089
S = 1.00
4312 reflections
310 parameters
$\Delta\rho_{max}$ = 1.09 e Å^{-3}
$\Delta\rho_{min}$ = −0.89 e Å^{-3}

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XTALDRAW* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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