Zeitschrift für Kristallographie, Bd. 132, S. 157–160 (1970)

The unit-cell contents of freudenbergite

By DUNCAN MCKIE and J. V. P. LONG

Department of Mineralogy and Petrology, University of Cambridge, Great Britain

(Received 3 April 1970)

Auszug

Neue Dichtebestimmungen und Elektronen-Mikrosondenanalysen ergaben für Freudenbergit $D = 3,95_6$ und als Inhalt der monoklinen Elementarzelle $(K^{+}_{0,01}Na^{+}_{1,98})(Mn^{2+}_{0,01}Nb^{5+}_{0,07}Fe^{3+}_{1,59}Ti^{4+}_{6,22})O^{2-}_{16}$. Die neuen Daten sprechen für die vermutete Identität von Freundenbergit mit Na_xTiO_2.

Abstract

Redetermination of the density of freudenbergite as 3.95_6 and new electron-probe microanalyses yield $(K_{.01}Na_{1.98})(Mn_{.01}Nb_{.07}Fe^{III}_{1.59}Ti_{6.22})O_{16}$ for the contents of the monoclinic unit-cell. The new data support the proposed structural identity with synthetic Na_xTiO_2.

MCKIE (1963) determined the unit-cell dimensions of freudenbergite ($a = 12.305$, $b = 3.822$, $c = 6.500$ Å, $\beta = 107.30°$) and made use of the density (4.3 g cm^{-3}) and chemical analyses given by FRENZEL (1961) for the same material to establish that the unit cell contained 18 oxygen atoms. WADSLEY (1964) commented on the close similarity of the powder pattern of freudenbergite to that of the synthetic sodium-titanium-dioxide 'bronze' $Na_{0.2}TiO_2$ and on the disparity between the density reported by FRENZEL for freudenbergite and that calculated on the assumption of similarity of structure with the synthetic 'bronze' (4.0 g cm^{-3}). BAYER and HOFFMANN (1965) reported that single-crystal studies on synthetic $Na_2O \cdot Fe_2O_3 \cdot 6\,TiO_2$ and $Na_2O \cdot Fe_2O_3 \cdot 7\,TiO_2$ were in agreement with MCKIE's results for freudenbergite and that the mean density determined for these two synthetic compositions was 3.9_5 g cm^{-3} indicating a content of 16 oxygen atoms per unit cell; their synthetic work demonstrates the existence of a solid solution $A_xB_yTi_{8-y}O_{16}$ with the freudenbergite structure and composition variable within wide limits for both the large cations A and the smaller titanium-substituting cations B.

Following the publication of WADSLEY's paper the density of natural freudenbergite was redetermined by the method outlined by MCKIE (1965) as 3.95_6 g cm^{-3} in close agreement with the mean value quoted for synthetic $Na_2O \cdot Fe_2O_3 \cdot 6$—$7\,TiO_2$ by BAYER and HOFFMANN (1965). Publication of this correction was to have been included in a paper on the crystal structure of freudenbergite, but completion of that has been delayed and it seems proper to clear this matter up without further delay.

Table 1. *Chemical composition of freudenbergite*

	FRENZEL I	FRENZEL II	MCKIE and LONG α	MCKIE and LONG β		α*	β*
K_2O	1.33	0.37	0.04	0.04	K^+	0.006	0.006
Na_2O	6.90	7.15	8.58	8.73	Na^+	1.963	1.987
MnO	0.26	0.14	0.14	0.14	Mn^{2+}	0.014	0.014
MgO	0.47	nil	(< 0.03)	(< 0.03)	Nb^{5+}	0.066	0.066
Nb_2O_5	2.73	2.97	1.24	1.24	Fe^{3+}	1.582	1.603
Fe_2O_3	18.94	20.19	17.81	18.15	Ti^{4+}	6.232	6.210
TiO_2	63.62	64.43	70.21	70.37	O^{2-}	16.000	16.000
Al_2O_3	0.47	nil	(< 0.10)	(< 0.10)			
SiO_2	2.03	2.03	(< 0.02)	(< 0.02)	$Na^+ + K^+$	1.969	1.993
H_2O^+	2.98	2.98	n.d.	n.d.	$R^{[6]}$	7.894	7.893
	99.73	100.26	98.02	98.67			

I, II wet chemical analyses by FRESENIUS and SCHNEIDER (FRENZEL, 1961).
α, β electron-probe microanalyses.
α*, β* unit-cell contents calculated to 16 oxygen atoms from columns α and β.

At this point it seemed advisable to redetermine the chemical composition of freudenbergite, the only piece of mineralogical data in FRENZEL's original description that had not been reinvestigated and corrected. Since the separation of a pure sample of freundenbergite appeared to be difficult if not impossible, as FRENZEL found, and in any case adequate material for a new wet chemical analysis was not available, the composition was redetermined by electron-probe microanalysis. The new analyses, performed on two grains, designated α and β, should be superior in every respect but one to the two analyses of admittedly impure samples published by FRENZEL (1961); the exception is that we were unable to determine H_2O^+, but it is notable that FRENZEL, for no stated reason, chose to ignore his determined content of 2.98% H_2O^+. The two new analyses together with FRENZEL's two analyses are shown in Table 1. While there is general similarity between the two pairs of analyses, the new pair show conclusively that the K_2O content of freudenbergite is very small, that the Nb_2O_5 content is rather less than half that indicated by FRENZEL's analyses and that TiO_2 is significantly higher. The presence of Mg, Al, and Si have not been confirmed by the electron-probe analyses; the amounts shown in columns α and β of Table 1 are generously estimated maxima and it is possible that these elements are absent, or present in no more than trace amounts. FRENZEL's arbitrary assignment of the 2.03% SiO_2 shown in his analyses to impurities was therefore correct. Our demonstration that significant amounts of Si are not present in freudenbergite is consistent with WADSLEY's equation of freudenbergite to synthetic Na_xTiO_2, the structure of which lacks tetrahedral sites.

The low totals of both the new analyses remain an unresolved problem. All elements of atomic number > 10 that seemed likely constituents were sought on the electron-probe microanalyser and found not to be present in significant amounts. The amount of this very rare mineral available to us makes it impossible to investigate the possibility that the substitution of OH^- for O^{2-} may account for the low totals. On the other hand, it must be recognized that while the statistics of the procedure used (SWEATMAN and LONG, 1969) make it unlikely that no other major elements are present, it is possible that this is so.

Calculation of unit-cell contents from the unit-cell dimensions of MCKIE (1963), the new density, and the new analyses leads to oxygen contents of 16.01 and 15.99 for analyses α and β respectively. WADSLEY's hypothesis that the unit-cell of freudenbergite, like that of synthetic Na_xTiO_2, contains 16 oxygen atoms is amply confirmed. Unit-cell contents calculated to 16 oxygen atoms are shown in columns α^* and β^* of Table 1. The unit-cell content of cations that commonly occur in six-fold coordination (Mn^{2+}, Nb^{5+}, Fe^{3+}, Ti^{4+}) shows a satisfactory approximation, 7.894 for α and 7.893 for β, to the number 8 as required for identification with the synthetic solid-solution series of BAYER and HOFFMANN. The unit-cell contents of freundenbergite can thus be formulated as $(K^+_{.01}\ Na^+_{1.98})\ (Mn^{2+}_{.01}\ Nb^{5+}_{.07}\ Fe^{3+}_{1.59}\ Ti^{4+}_{6.22})\,O^{2-}_{16}$, or in general terms as $A_{1.99}B_{7.89}O_{16}$.

References

G. BAYER und W. HOFFMANN (1965), Über Verbindungen vom Na_xTiO_2-Typ. Z. Kristallogr. **121**, 9–13.

G. FRENZEL (1961), Ein neues Mineral: Freudenbergit ($Na_2Fe_2Ti_7O_{18}$). Neues Jahrb. Min., Monatsh., 12–22.

D. MCKIE (1963), The unit-cell of freudenbergite. Z. Kristallogr. **119**, 157–160.

— (1965), The magnesium aluminium borosilicates: kornerupine and grandidierite. Mineral. Mag. **34**, 346–357.

T. R. SWEATMAN and J. V. P. LONG (1969), Quantitative electron-probe microanalysis of rock-forming minerals. J. Petrol. **10**, 332–379.

A. D. WADSLEY (1964), The possible identity of freudenbergite and Na_xTiO_2. Z. Kristallogr. **120**, 396–398.