ISOMORPHOUS REPLACEMENTS IN HARKERITE AND THE RELATION OF SAKHAITE TO HARKERITE

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ABSTRACT

The isomorphous replacements $BO_3OH^{4-} \rightleftharpoons SiO_4^{4-}$ and $[(OH)_2.H_2O]^{2-} \rightleftharpoons CO_3^{2-}$ have resulted in a proposed new ideal formula for harkerite, $8[Ca_{48}Mg_{16}Al_3(BO_3)_{13}(CO_3)_{19^-}(SiO_4)_{14}(OH)_2Cl_2.2H_2O]$, based on the analyses of earlier workers. The isomorphous replacement $[(OH)_2.H_2O]^{2-} \rightleftharpoons CO_3^{2-}$ is also suggested as a means of rationalising the formula of jennite, the new ideal formula being $[(Ca, Na_2)_9Na(SiO_3)_3(Si_2O_7)(OH)_{2^-}(H_2O)(OH)_5.7H_2O]$. An examination of a relationship between sakhaite and harkerite leads to a recalculated formula for sakhaite, $[Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{13}(OH)_4Cl_4.6H_2O]$.

Harkerite was first described by Tilley (1951) after its discovery in a skarn deposit in Skye, and at present this is the only known occurrence, although Pertsev's (1961) finding of sakhaite which he initially identified as harkerite is worthy of note. According to Henry (*in* Tilley 1951) harkerite is cubic with $a = 29.53 \pm 0.01$ Å. There is a pseudocell with edge $a/2$. The specific gravity is 2.959 at 20° C. Taking the pseudocell as 14.76 Å, Tilley found the molecular weight per pseudocell to be 5731 and the number of anions to be 157 (O,OH,Cl). Using 156 as the number of anions, Tilley calculated the formula $20CaCO_3.Ca_{28}Mg_{15.5}Al_{3.5^-}Fe^{2+}_{0.5}Fe^{3+}_{0.5}(Si_{13}B_{11})(O,OH,Cl)_{96}$ in which tetrahedral co-ordination of boron was assumed and assigned to a similar structural position as silicon, the ratio (Si,B):(O,OH,Cl) being 1:4. It was acknowledged that the formula did not represent the analysis well.

If we take the pseudocell as 14.765 Å the molecular weight of the pseudocell becomes 5737.0 and the number of (O,OH,Cl) contained in it is 157.70. Since the nearest integer is 158, the analysis of Vincent (*in* Tilley 1951) was recalculated on this basis (Table VI), the only difference being that the minor constituent MnO has been included since there appears to be no reason for it being omitted.

A more recent analysis of the Skye harkerite by Ostrovskaya *et al.* (1966) also bases the analysis on a total of 158 (O,OH,Cl) and the two sets of results are compared in Table 1. The considerable differences in the analyses are discussed later in this paper. It should be noted that the maximum possible magnetite calculated from 0.85 percentage Fe_2O_3 amounts to 1.23 percent, and since in the original analysis of Vincent (*in* Tilley 1951) the magnetite was removed by high density liquids it seems likely that most of the ferric iron occurs in the harkerite structure

TABLE 1. CHEMICAL ANALYSES OF HARKERITE

	(I. V. Nikitina, analyst, *in* Ostrovskaya *et al.* 1966)		(H. C. G. Vincent, analyst, *in* Tilley 1951)	
Component	Wt. %	Atoms per 158(O, OH, Cl)	Wt. %	Atoms per 158(O, OH, Cl)
SiO_2	12.74	Si 12.10	14.17	Si 13.52
B_2O_3	9.20	B 15.08	7.77	B 12.79
Al_2O_3	2.51	Al 2.81	2.84	Al 3.20
Fe_2O_3	—	Fe^{3+} —	0.85	Fe^{3+} 0.61
FeO	0.87	Fe^{2+} 0.69	0.46	Fe^{2+} 0.37
MnO	n.d.	Mn^{2+} —	0.02	Mn^{2+} 0.02
MgO	11.32	Mg 16.02	11.15	Mg 15.85
CaO	46.31	Ca 47.12	46.23	Ca 47.24
CO_2	13.90	C 18.02	14.94	C 19.45
Cl	1.26	Cl 2.03	1.36	Cl 2.20
H_2O^+	1.92	H 12.16	0.81	H 5.16
H_2O^-	—	— —	0.11	— —
		O 155.97		O 155.80
	100.03		100.71	
$-O = Cl$	0.27		0.31	
	99.76		100.40	

and not as magnetite impurity. However, since unremoved magnetite is likely to be low, any effect on the formula would be minimal.

For both sets of figures divisions may be made in accord with normal crystallochemical principles whereby atoms of similar size and co-ordination are grouped together (Table 2). Three groups of cations will be recognized; group I—the small atoms of C, B and Si; group II—Ca, Mn, Fe^{2+}, Mg and Fe^{3+}; group III—Al, which is of intermediate size.

Clearly the ideal number of atoms in group II is 64, but a subdivision may be assumed in this group since the ratio (Ca + Fe):Mg is very close to 48:16 which are reasonable equipoint numbers for a complex cubic

TABLE 2. CONSTITUENT ATOMS OF HARKERITE GROUPED ACCORDING TO SIZE

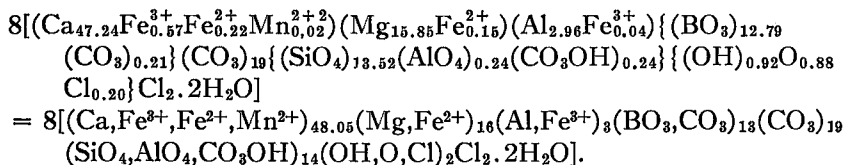| Element	Analysis due to Ostrovskaya *et al.* (1966)	Analysis due to Tilley (1951)
Group I { C B Si	18.02 15.08 12.10 } 45.20	19.45 12.79 13.52 } 45.76
Group III Al	2.81	3.20
Group II { Fe^{3+} Mn Mg Fe^{2+} Ca	— n.d. 16.02 0.69 47.12 } 63.83	0.61 0.02 15.85 0.37 47.24 } 64.09

mineral. The average Al content is 3.00. Group I shows the greatest differences but if the minor excess of 0.20 Al is transferred to group I, the total becomes 45.96—significantly 46. The figures from the analysis of Ostrovskaya *et al.* (1966) still show a major deficiency in this group compared with our assumed ideal of 46 atoms, but their analysis also shows a great excess of hydrogen atoms when compared with the analysis of Tilley. In some way therefore, these excess hydrogen atoms must replace the small cations C, B and Si and thus bring the total number of atoms associated with these various cations up to the ideal requirements of 46.

On the basis of chemical analysis, x-ray data, infrared spectroscopy and thermogravimetric data, Ostrovskaya *et al.* (1966) represented the ideal formula of harkerite as $Ca_{48}Mg_{16}Al_3(BO_3)_{15}(SiO_4)_{12}(CO_3)_{18}$-$(OH)_6Cl_2 . 3H_2O$. Using their chemical analysis, and taking into consideration the analytical difficulties in complete determination of Al_2O_3 thus allowing for a slight deviation of Al from the stoichiometric value of 3, the total number of cations $(Ca + Mg + Fe^{2+} + Al)$ is 67. The equipoint numbers of $48(Ca + Fe^{2+} + Mg):16Mg:3Al$ are consistent with this interpretation and the following crystallochemical formula results, using integers where obvious:

$$8[(Ca_{47.25}Fe^{2+}_{0.69}Mg_{0.06})Mg_{16}Al_3(BO_3)_{15}(SiO_4)_{12}(CO_3)_{18}(OH)_6Cl_2 . 3H_2O].$$
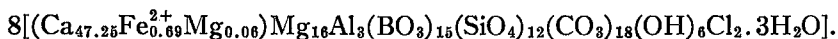
The omission of minor Fe^{2+} and substituting Ca for minor Mg yields their proposed ideal formula above.

In the following formula for Tilley's (1951) analysis in which the elements are generally grouped according to ionic radii, Fe^{3+} has been arbitrarily included with Ca so that Mg is as near to 16 as possible,

$$8[(Ca_{47.24}Fe^{3+}_{0.57}Fe^{2+}_{0.22}Mn^{2+2}_{0.02})(Mg_{15.85}Fe^{2+}_{0.15})(Al_{2.96}Fe^{3+}_{0.04})\{(BO_3)_{12.79}$$
$$(CO_3)_{0.21}\}(CO_3)_{19}\{(SiO_4)_{13.52}(AlO_4)_{0.24}(CO_3OH)_{0.24}\}\{(OH)_{0.92}O_{0.88}$$
$$Cl_{0.20}\}Cl_2 . 2H_2O]$$
$$= 8[(Ca,Fe^{3+},Fe^{2+},Mn^{2+})_{48.05}(Mg,Fe^{2+})_{16}(Al,Fe^{3+})_3(BO_3,CO_3)_{13}(CO_3)_{19}$$
$$(SiO_4,AlO_4,CO_3OH)_{14}(OH,O,Cl)_2Cl_2 . 2H_2O].$$

In the actual structure it is doubtful whether Fe^{3+} would replace Ca since there is ample Mg available (which has a larger ionic radius) to make up the ideal site requirements of 48 in the Ca group. If this does happen, the Fe^{3+} could be readily accommodated in the vacant Mg positions. The scheme of the various replacements in the crystallochemical formula is straight-forward, since at this stage, no unconventional type of isomorphism is considered. Minor AlO_4^{5-} substituting for SiO_4^{4-} is accompanied by an equivalent CO_3OH^{3-}, thus preserving charge balance. The substitution of Ca (or Mg) by Fe^{3+} causes a replacement of OH by O, but exact correspondence cannot be shown in the formula since

(1) a minor amount of CO_3^{2-} substitutes for BO_3^{3-} and hence reduces the cationic charge requirements, and (2) the first group (Ca, Fe^{3+}, Fe^{2+}, Mn^{2+}) has a minor excess over the stoichiometric value of 48 atoms. Neglecting the minor replacements outlined above, the ideal formula for Tilley's harkerite analysis would be $8[Ca_{48}Mg_{16}Al_3(BO_3)_{13}(CO_3)_{19}(SiO_4)_{14}$-$(OH)_2Cl_2.2H_2O]$. This compares with that proposed by Ostrovskaya $et\ al.$ (1966), namely $8[Ca_{48}Mg_{16}Al_3(BO_3)_{15}(CO_3)_{18}(SiO_4)_{12}(OH)_6Cl_2.3H_2O]$.

In order to convert the latter formula into the newly proposed one using Tilley's (1951) data, two different types of isomorphous substitution must be made: (a) replacement of $2BO_3OH^{4-}$ by $2SiO_4^{4-}$ and (b) replacement of $[(OH)_2.H_2O]^{2-}$ by the dimensionally equivalent CO_3^{2-}. The resultant formula is $8[Ca_{48}Mg_{16}Al_3(BO_3)_{13}(CO_3)_{19}(SiO_4)_{14}(OH)_2Cl_2.2H_2O]$. Replacement of SiO_4^{4-} by BO_3OH^{4-} is not uncommon but is restricted to minerals containing isolated SiO_4^{4-} groups in their structures (Christ 1959). The replacement $CO_3^{2-} \rightleftharpoons [(OH)_2.H_2O]^{2-}$ has never been suggested to explain variations in the analyses of any mineral species. It is suggested here because of its similarity to the replacement of BO_3^{3-} in the $B_2O_4OH^{3-}$ groups by $(OH)_3^{3-}$ found in the recently discovered mineral hydroxyl-szaibelyite (Grigor'ev $et\ al.$ 1966, Grigor'ev & Nekrasov 1966), $Mg_2(B_{2-x}H_{3x}O_4OH)OH$, which is a variety of the common skarn mineral szaibelyite, whose ideal formula is $Mg_2(B_2O_4OH)OH$, although these workers also mention the possibility of replacement of B by Mg. However, only the former interpretation is consistent with our recalculated analyses.

It should be noted that the harkerite formula deduced shows a maximum number of SiO_4^{4-} groups since if such groups are present, tetrahedral sites are available to accommodate B and C atoms, whereas of course, excess Si atoms could not enter empty trigonal sites. The synthetic apatite-like compound $Pb_5(SiO_4)(BO_3)_2$ has two-thirds of the tetrahedral positions of an apatite structure replaced by trigonal BO_3^{3-} groups, so our case may well be analogous hence explaining the different SiO_4^{4-} and BO_3^{3-} ratios.

It is relevant to mention here that another formula for harkerite (Hey 1955, p. 212) $8[Ca_{48}Mg_{16}B_{12}(Si, Al)_{16}O_{84}(OH, Cl)_{12}(CO_3)_{20}]$ was proved to be in error on recalculation of Tilley's (1951) analysis. Apparently the five hydroxyls from the analysis table had been taken to read as five water molecules thus giving ten hydroxyls, which together with the two chlorines would produce a total of twelve (OH, Cl). Because of this incorrect interpretation, the balanced formula with O = 84 and (OH, Cl) = 12 would be $8[Ca_{48}Mg_{16}B_{12}Si_8Al_8O_{84}(OH, Cl)_{12}(CO_3)_{20}]$ whereas in fact Si is about 13 and Al about 3 on the 156(O, OH, Cl) basis that was used.

TABLE 3. SAKHAITE ANALYSES

Component	1	2	3	4	Weight % 5	6	7	8	9
CaO	50.18	49.55	50.53	50.50	49.83	49.81	50.17	50.24	51.08
MgO	12.54	12.35	12.16	12.19	11.94	11.98	12.07	12.05	12.24
B_2O_3	17.65	18.07	17.77	17.76	18.17	18.16	17.96	18.20	18.50
CO_2	14.33	14.87	14.43	14.42	14.96	14.95	14.69	14.77	13.36
H_2O^+	2.75	2.52	2.75	2.77	2.52	2.53	2.64	2.69	2.74
Cl	2.63	2.73	2.65	2.65	2.75	2.74	2.70	2.65	2.69
SiO_2	0.25	0.25	—	—	—	—	—	—	—
Al_2O_3	0.24	0.25	0.31	0.31	0.33	0.33	0.32	—	—
FeO	0.31	0.33	—	—	0.05	0.05	0.025	—	—
MnO	—	0.05	—	—	0.04	0.04	0.02	—	—
Na_2O	—	0.04	—	—	0.03	0.03	0.015	—	—
K_2O	—	0.03	—	—	—	—	—	—	—
Total	100.88	101.04	100.60	100.60	100.62	100.62	100.61	100.60	100.61
$-O = Cl$	0.59	0.62	0.60	0.60	0.62	0.62	0.61	0.60	0.61
Total	100.29	100.42	100.00	100.00	100.00	100.00	100.00	100.00	100.00

1 and 2. Analyses 1 and 2 *in* Ostrovskaya *et al.* (1966) before deduction of impurities.
3. Analysis 1 recalculated to 100 after deduction of Al_2O_3 as spinel, $MgAl_2O_4$, and SiO_2 as clinohumite*, $Mg_9(SiO_4)_4(OH)_2$.
4. Analysis 1 recalculated to 100 after deduction of Al_2O_3 as spinel and SiO_2 as forsterite, Mg_2SiO_4.
5. Analysis 2 recalculated to 100 after deduction of Al_2O_3 as spinel and SiO_2 as clinohumite*.
6. Analysis 2 recalculated to 100 after deduction of Al_2O_3 as spinel and SiO_2 as forsterite.
7. Average of columns 3, 4, 5 and 6.
8. Calculated composition for $Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{18}(OH)_4Cl.6H_2O$.
9. Calculated composition for $Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{18}(OH)_8Cl.4H_2O$.
*The formula of clinohumite is usually given as $Mg_9(SiO_4)_4(F, OH)_2$ but we have used the formula $Mg_9(SiO_4)_4(OH)_2$ since no fluorine was reported in the analysis.

Other formulas for harkerite $Ca(Mg, Al)(Si, BH)O_4 . CaCO_3$, $Z = 24$, (Strunz 1957, p. 221) and $Ca_4Mg(SiO_4)(BO_3)(CO_3)OH$, $Z = 96$ (Pova-rennykh 1966, p. 313) have been rejected on the basis of our recalcula-tions.

Since the isomorphous replacements $CO_3{}^{2-} \rightleftharpoons [(OH)_2 . H_2O]^{2-}$ has been suggested, the question of how the carbonate groups are accommodated in the new mineral jennite (Carpenter *et al.* 1966) was re-examined. In jennite there are no deficiencies in the Si positions and there are no other small atoms, but in some way 0.36 $CO_3{}^{2-}$ per cell must be accommodated. The replacement schemes as outlined above could satisfactorily explain the incorporation of these carbonate groups. Analysed jennite then becomes $[(Ca, Na_2)_9Na(SiO_3)_3(Si_2O_7)\{(OH)_{1.28}(H_2O)_{0.64}(CO_3)_{0.36}\} (OH)_5 . 7H_2O]$, more generally as $[(Ca_{9-x}Na_{2x})Na(SiO_3)_3(Si_2O_7)\{(OH)_{2-2y}(H_2O)_{1-y}(CO_3)_y\}-(OH)_5 . 7H_2O]$, and an ideal formula of $[(Ca,Na_2)_9Na(SiO_3)_3(Si_2O_7)(OH)_2-(H_2O)(OH)_5 . 7H_2O]$. At this stage lack of further analyses does not permit the interpretation of other formulas in a similar way, but since two rather complex formulas have been solved satisfactorily, it is suggested that the replacement $CO_3{}^{2-} \rightleftharpoons [(OH)_2H_2O]^{2-}$ is another means by which carbonate groups may generally be included in hydroxyl-bearing silicate lattices, although no actual examples have as yet been reported.

The formula of sakhaite was recalculated in an attempt to determine whether a relationship existed between sakhaite and harkerite. Our conclusions are largely in agreement with those of Ostrovskaya. Table 3 shows the analyses of sakhaite by Nikitina (*in* Ostrovskaya *et al.* 1966). Both analyses have been recalculated after deduction of impurities; in both cases Al_2O_3 was removed as spinel but the uncertainty in the forsterite:clinohumite ratio necessitated the calculations.

The table shows that the formula of sakhaite is nearer to $[Ca_{48}Mg_{16}-(BO_3)_{28}(CO_3)_{18}(OH)_4Cl_4 . 6H_2O]$ than to $[Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{18}(OH)_8-Cl_4 . 4H_2O]$. It should be noted that this new formula contains 46 trigonal groups ($CO_3{}^{2-}$ and $BO_3{}^{3-}$), whereas in the revised harkerite formula (based on Tilley's (1951) analysis) there are 46 trigonal and tetrahedral groups ($BO_3{}^{3-}$, $CO_3{}^{2-}$ and $SiO_4{}^{4-}$). Although no explanation is offered, it may well be that the replacement is somewhat akin to that of $Si_2O_7{}^{6-} \rightleftharpoons 2BO_3{}^{3-}$ (Mamedov & Belov 1964).

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