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Further studies on winchite from the type locality

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Abstract

An extensive search for winchite [$CaNaMg_4AlSi_8O_{22}(OH)_2$] by microprobe anlyses of violet amphiboles obtained from the type locality has failed to identify any sodic calcic amphiboles. In particular, none is near to either the original or the theoretical end-member composition of winchite. The violet amphiboles are generally magnesio-arfvedsonite to magnesio-riebeckite, sometimes manganoan and titanian, but always alkali amphiboles. In addition, the Mn-rich amphiboles have C-group totals significantly lower than the 5.00 expected in the ideal amphibole formula. Colorless tremolite is present in some of the violet amphibole-bearing rocks. We suggest, but have not conclusively proved, that the original analysis of winchite was in error.

Introduction

The amphiboles from the manganese ore mine of Kajlidongri, Jhabua district, Madhya Predesh, India have been investigated for many years. From this locality, Mr. H. J. Winch first discovered the violet blue amphibole subsequently analyzed and named winchite by Fermor (1904, 1909). This analysis was halfway between tremolite and glaucophane and approached $CaNaMg_4AlSi_8O_{22}(OH)_2$. Other analyzed amphiboles from this locality include tremolite (Nayak, 1962), magnesio-arfvedsonite (Nayak and Leake, 1975), tirodite (Lahiri, 1971) and manganoan eckermannite (Lahiri, 1971); all these names are in accordance with recommendations of the International Mineralogical Association (Leake, 1978). However, recent investigations of the violet amphiboles have not yielded an analysis similar to that of the original winchite with respect to Ca and Na contents—critical features of the end-member winchite formulae $CaNaMg_4AlSi_8O_{22}(OH)_2$ (alumino-winchite) and $CaNaMg_4Fe^3Si_8O_{22}(OH)_2$ (ferri-winchite) and their equivalent ferrous (replacing Mg) end-members.

In an attempt to resolve this problem, Nayak and Leake (1975) carried out superior wet-chemical analyses of highly purified violet amphibole collected from the same mineral assemblage at Kajlidongri as the original winchite. However, an alkali amphibole analysis, magnesio-arfvedsonite, not a sodic-calcic composition, was obtained. In particular, 1.52% CaO and 7.74% Na_2O was obtained instead of the 7.64% CaO and 2.89% Na_2O originally reported by Fermor (1909; analyses A and B reproduced in Table 1). However, both the original material and the newer material were highly zoned and the possibility existed that either the cores or the margins of the violet amphiboles might approximate to the material analyzed by Mr. T. R. Blyth for Fermor. Fermor (1909, p. 155) describes in detail the separation procedure he adopted and it is clear he was particularly concerned to remove the heavy black Mn-oxide braunite; this might have ensured that the lightest fraction was preferentially concentrated for analysis. Accordingly, in this study microprobe analyses have been carried out on a wide range of samples from the Kajlidongri mine in search of any amphibole which might chemically resemble the original winchite analysis. Both the mineral assemblage from which the original winchite was collected and other similar mineral assemblages were examined. We report rep-

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resentative amphibole analyses selected from a very large number determined on a variety of samples.

Procedures

The analyses were carried out on a Microscan Mark V equipped with an energy-dispersive system, using a combination of pure metal and silicate standards.

Because previous wet-chemical analyses have shown that the amphiboles from this locality have essentially all their iron in the ferric state, this has also been assumed for the present samples. Thus Nayak and Leake (1975) showed 12.09% Fe_2O_3 and 0.10% FeO (see B in Table 1), in agreement with Lahiri (1971) who reported 6.00% Fe_2O_3 and 0.13% FeO. The question of the oxidation state of the manganese is more difficult. The presence of abundant braunite and bixbyite, hollandite with 63% MnO_2, 4% MnO (Lahiri, 1971), and the common occurrence of piemontite and aegirine indicates that some Mn^{3+} probably occurs. In the absence of any means of rationally allocating Mn between different oxidation states by probe work, the Mn in the amphiboles has been reported in the conventional form as MnO, although we recognize that this is not proven.

Mineral assemblages

The colorless to deeply pleochroic violet, lilac, violet-red to red amphiboles of Kajlidongri occur in quartzites and schists containing various combinations of quartz, calcite, aegirine, hollandite, piemontite, phlogopite, hematite, bixbyite, braunite, and complex Mn oxides. The pelites commonly contain pure albite, and their metamorphic grade is equivalent to either the chlorite or low-biotite zone. Further background information is given by Fermor (1909), Nayak (1962), Lahiri (1971), and Nayak and Leake (1975). Pleochroic and birefringence zoning together with optical anomalies (described in detail by Fermor, 1909) were characteristic of the original winchite, and we have also found such properties in all the samples described. Brief descriptions of selected representative samples follow.

Sample 2 contains (up to 1 cm) prismatic, nearly colorless amphiboles with bluish rims. Between these prisms are coarse albite ($Ab_{99.5-100}$), pockets of manganoan (4.80% MnO) phlogopite, and a little (1%) prismatic hollandite. The amphibole is zoned from a magnesio-riebeckite (Table 1; 2c) to a magnesio-arfvedsonite (2r), and it contains fine albite inclusions, normally clustered near the center of the crystal. Analysis 2r shows the highest Ca content of any sample analyzed yet it only has 2.83% CaO.

Sample 6 consists of 35% fine-grained quartz-albite (Ab_{100}) groundmass with 13% calcite in clots 0.2 mm in diameter, a little (4%) opaque oxide, and 48% large (up to 5 mm) zoned amphiboles irregularly radiating through the rock. The amphiboles are pleochroic lilac to pale pink, and sometimes (not always) have deep pink titanian manganoan magnesio-arfvedsonite rims (6r). Inclusions of calcite and albite are common. The chemical zoning is rather erratic, but the pink rims (6r) are generally richer in Ti, Mg, K, and Mn and poorer in Al, Ca, and Fe than the cores (6c). However, one crystal with 4.95% TiO_2 in its core (6c) has rim compositions varying from 0.50 to 5.82% TiO_2. Such high Ti contents are remarkable and exceed the minimum Ti of 0.50 (ca. 5% TiO_2) in kaersutite. The composition is similar to that of "juddite", except that Ti is not a necessary feature of "juddite" (now referred to as manganoan magnesio-arfvedsonite).

Sample 7 is composed of about 40% zoned deep red amphibole with 20% pure albite (Ab_{100}) and 40% manganese oxide, probably largely braunite and bixbyite (10% SiO_2, 2% Fe_2O_3, 90% Mn_2O_3). The amphibole is erratically zoned. For instance, some crystals have cores richer in Ti than their rims, whereas others show the reverse relationship. In general, however, the cores are richer in Na_2O (av. 9.44% Na_2O), CaO (0.48%), and Fe_2O_3 (10.83%), and poorer in TiO_2(0.05 to 0.90%), MnO (5.05%), and K_2O (1.91%) than the rims, which reach 1.24% TiO_2, 6.94% MnO, and 2.19% K_2O. Analysis 7c is typical and is a manganoan magnesio-arfvedsonite (formerly termed "juddite").

Sample 11 contains 34% colorless prismatic amphibole (pale green in hand specimen), whose zoning is indicated by varying birefringence. It is embedded in 59% fine-grained matrix of quartz, albite (Ab_{100}), and about 7% iron oxide, probably hematite (98.06% Fe_2O_3, 1.53% MnO, 0.40% TiO_2 and 0.64% SiO_2). Compositionally, the amphibole is a crossite or magnesio-riebeckite, depending upon the precise Fe_2O_3 content. (Because the new amphibole nomenclature [Leake, 1978] requires a knowledge of the Fe^{3+} and Fe^{2+} contents, names assigned based on probe data alone are sometimes ambiguous.) Analyses show that a typical core (11c) has slightly lower Ti and Mn contents than the rim. Minute inclusions of quartz and albite, which mimic the amphibole crystal form, are especially common in the cores of these crystals.

Sample 14 is composed of approximately 50%

Table 1. Chemical analyses of representative Kajlidongri amphiboles.

	A	B	2c	2r	6c	6r	6c'	6r'	6r'	7c	11c	14	21r
SiO_2	55.64	57.31	58.15	57.23	57.65	56.49	56.46	56.79	56.42	56.03	56.32	58.07	56.98
Al_2O_3	1.08	1.19	0.86	0.61	0.82	0.92	0.87	0.84	0.84	1.27	1.00	1.37	0.75
TiO_2	0.00	0.01	0.00	0.00	0.27	5.60	4.95	5.82	2.60	0.78	0.00	0.00	0.00
Fe_2O_3	7.06	12.09	13.60	8.35	11.35	8.05	9.28	9.11	10.84	10.62	15.21	2.07	13.35
MnO	0.77	0.62	0.31	0.60	0.63	5.94	5.61	5.78	2.81	6.31	0.27	0.19	0.47
MgO	22.09	16.04	16.41	18.99	17.30	9.49	9.94	9.27	12.74	9.59	15.92	23.15	16.21
CaO	7.64	1.52	1.36	2.83	1.69	0.93	0.64	0.65	0.99	0.47	1.26	12.57	1.20
Na_2O	2.89	7.74	7.91	7.58	8.75	9.98	10.23	10.25	9.32	9.54	7.44	0.87	7.97
K_2O	0.98	0.95	0.60	1.19	0.87	0.93	0.79	0.77	1.05	2.19	0.38	0.00	0.49
Total	101.38	99.66	99.20	97.38	99.33	98.33	98.77	99.28	97.61	96.80	97.80	98.29	97.42
							Formula to 23(O)						
Si	7.70	8.01	7.99	7.98	7.93	7.99	7.96	7.97	7.98	8.14	7.88	7.86	7.98
Al_T	0.17	0.00	0.01	0.02	0.07	0.01	0.04	0.03	0.02	0.00	0.12	0.14	0.02
Al_c	0.00	0.19	0.13	0.08	0.07	0.14	0.11	0.11	0.12	0.22	0.05	0.08	0.10
Ti	0.00	0.00	0.00	0.00	0.03	0.60	0.53	0.61	0.28	0.09	0.00	0.00	0.00
Fe^3	0.73	1.27	1.41	0.88	1.18	0.86	0.99	0.96	1.15	1.16	1.60	0.21	1.41
Mn	0.09	0.07	0.04	0.07	0.07	0.71	0.67	0.69	0.34	0.78	0.03	0.02	0.06
Mg	4.55	3.34	3.36	3.95	3.55	2.00	2.09	1.94	2.69	2.08	3.32	4.67	3.38
Ca	1.13	0.23	0.20	0.42	0.25	0.14	0.10	0.10	0.15	0.07	0.19	1.82	0.18
Na_B	0.77	1.77	1.80	1.58	1.75	1.86	1.90	1.90	1.85	1.93	1.81	0.18	1.82
Na_A	0.00	0.33	0.31	0.47	0.58	0.88	0.90	0.89	0.71	0.76	0.22	0.05	0.34
K	0.17	0.17	0.11	0.21	0.15	0.17	0.14	0.14	0.19	0.41	0.07	0.00	0.09
ΣT	7.87	8.01	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.14	8.00	8.00	8.00
ΣC	5.37	4.88	4.94	4.98	4.90	4.31	4.39	4.31	4.58	4.33	5.00	4.98	4.95
ΣB	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ΣA	0.07	0.50	0.42	0.68	0.73	1.05	1.04	1.03	0.90	1.17	0.29	0.05	0.43

Suffixes c and r at the top indicate core and rim. A is original winchite from Fermor (1909) and includes 3.09% loss on ignition, 0.14% H_2O–; B is from Nayak and Leake (1975) and includes 0.10% FeO, 2.09% H_2O giving 0.01 Fe^{2+} in formula unit.

quartz, 18% piemontite, 10% calcite, 10% manganoan phlogopite, 8% amphibole, 2% Mn oxide (82.1% Mn_2O_3, 9.6% Fe_2O_3, 10.0% SiO_2), and 2% pure Mg talc. The calcite contains about 55% CaO, 1% MgO, 0.5% MnO, and minor SrO. The piemontite is irregularly zoned, often with slightly more Fe and Mn and less Mg in the rim than the core. The tremolite (14) varies little in composition. It often occurs as crudely radiating prisms in the rock and in irregular veins, which is consistent with a metasomatic origin.

Sample 21 contains about 30% calcite, 33% quartz, and 27% hollandite with small amounts (5%) of pale violet amphibole and 5% granular aegirine that is filled with patchy, opaque minerals. The amphibole rim (21r) is a magnesio-riebeckite that has slightly more Na, K, Ca, and Mn than the core.

Discussion

Microprobe analyses of the violet amphiboles from Kajlidongri have confirmed the presence only of calcic (tremolite) and alkali amphiboles. Although there is a variety of violet amphiboles, with optical properties identical to the original winchite, all are alkali amphiboles. None approach either the theoretical composition of winchite or the composition reported by Fermor (1909), as is shown by Figure 1. Either we have not discovered a sample of the sodic-calcic amphibole described by Fermor or the original analysis

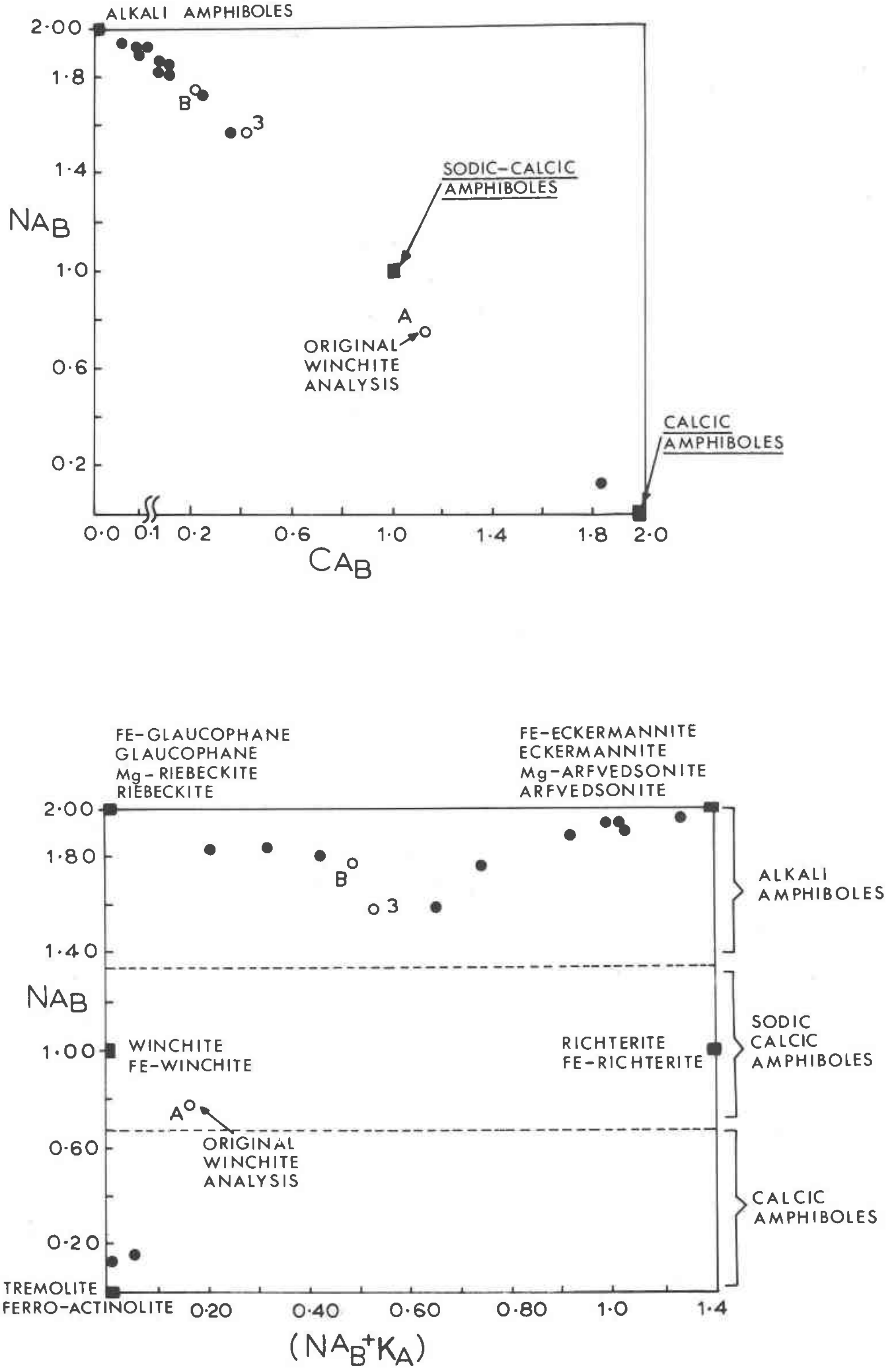

Fig. 1. Plots of representative analyses of amphiboles from Kajlidongri (Table 1). Open circles are wet-chemical analyses; solid spots, microprobe data. The sample numbered 3 is from Lahiri (1971). Only end-member amphiboles with 8 Si in the standard formula are named specifically.

was in error. It seems unwise to conclude that the original analysis was definitely in error, especially in view of the erratic chemical zoning and the presence of veins of various mineralogies (Lahiri, 1971) that we attribute to metasomatism. Nevertheless, the balance of evidence is clearly in favor of an error in the original analysis.

Fermor's (1909, p. 155) description of the separation procedure shows that the lightest fraction was selected in order to exclude Mn oxides, and that the calcite present was removed with dilute acid. However, inclusions of calcite may not have been completely removed; indeed, if they were similar to those in our sample 6, this would have been difficult. To explain the excess Ca in Fermor's analysis, about 9% calcite impurity is needed. This alone would cause 4% loss on ignition and would not explain the low Na_2O; thus, it seems unlikely to be the correct explanation. Older analyses are most often erroneous in alkalies because of the difficulties of the method and impurities in the available chemicals. Furthermore, the analysis has unsatisfactory features: the sum of the tetrahedral group is only 7.70, whereas the sum of the C group is much too high. The possibility that a mixture of magnesio-arfvedsonite and tremolite was analyzed is rejected as inconsistent with the careful original description. Accordingly, the most likely explanation is analytical error with or without calcite contamination.

A feature of the analyzed Mn-rich amphiboles is a consistently low C-group total, ranging down to below 4.30 instead of the theoretical 5.00. The analyses have been carefully checked and rechecked for errors and the presence of additional elements that might produce such low C-group totals. It is significant that none of the Mn-poor amphiboles has a C-group total below 4.88. If we suppose that the assumed H_2O content (ca. 2%) in calculating to 23(O) [$=O_{22}(OH)_2$] is too high, recalculation to a lower H_2O content increases the C-group total, but leads to large excesses above 8.00 in the Si. The Si of 7c is already high, which suggests that it has substantially more H_2O than 2%. Precise and carefully checked analyses have confirmed that H_2O does reach about 3% in some amphiboles (Kemp and Leake, 1975), probably in part due to H_3O^+ in the A site. The calculated deficiency in the C-group total of 7c is therefore likely to be a minimum. In summary, high H_2O is probably not the explanation of the low C-group totals, nor is the allocation of Mn to MnO (because allocation to Mn_2O_3 increases the deficiency).

There are several possible explanations for the low C-group totals apart from analytical error. The allocation of ions in amphiboles is a formal mathematical procedure not necessarily corresponding to reality. For instance, a very substantial proportion (>60%) of the 1217 analyzed amphiboles examined by Leake (1968) have C-group totals well over 5.00, with some ranging up to 5.40 in otherwise apparently "good" analyses. Where these extra ions are accommodated is quite uncertain. Also certain amphiboles might have vacancies in some positions. In our analyses with the low C-group totals, the elements Na and K usually exceed the supposed space available in the A position. They might be partly accommodated in the M_1, M_2, and M_3 positions of the C-group, with their larger size being tolerated structurally by the presence of vacancies. Alternatively, the vacancies might arise from the incorporation of atypically large percentages of Mn^{2+}, which is a significantly larger ion (ionic radius 0.82Å) than Al^{VI} (0.53Å), Fe^{3+} (0.65Å), Mg^{2+} (0.72Å), or Fe^{2+} (0.77Å), the normal major constituents of the C-group. Some evidence supports this latter deduction because Figure 2 shows a good positive correlation between Mn content and deficiency in the C-group total. Structural accommodation of increasing amounts of Mn might require the omission of ions from adjoining sites. There is no such correlation with Na or Ti contents.

Another possibility is that the crystal structure is unusual. The scarcity of natural winchite compositions is probably a consequence of an immiscibility gap between tremolite and glaucophane. The curious zoning and optical properties of these amphiboles suggest an unusual structure, but this has not been investigated.

Although these results should effect no changes in the nomenclature of amphiboles, the question arises as to what is the nearest analyzed sample to the theoretical end-member called winchite, *e.g.*, $CaNaMg_4AlSi_8O_{22}(OH)_2$. Bearing in mind the need for an ideal amphibole formula to approach eight Si atoms, one Ca, one Na, and zero (Na + K) in the A position, there appear to be no published analyses that *closely* match the end-member composition. Even the original analyses with Si 7.70 and Na 0.77 was not very close. Analyses 82 and 950 (see Leake, 1968 for numbers and documentation) from a syenite in the Harz Mountains, Germany, and from a fault fissure in gneiss near Disko, Greenland, have respectively Si 7.75, Ca 1.08, Na_B 0.92, Na + K 0.40 and Si 7.76, Ca 0.90, Na_B 0.95, Na + K 0.17 in the standard formula. The latter (analysis 950) has a high total (100.98), high P_2O_5 (0.22) suggesting apatite inclusions (and

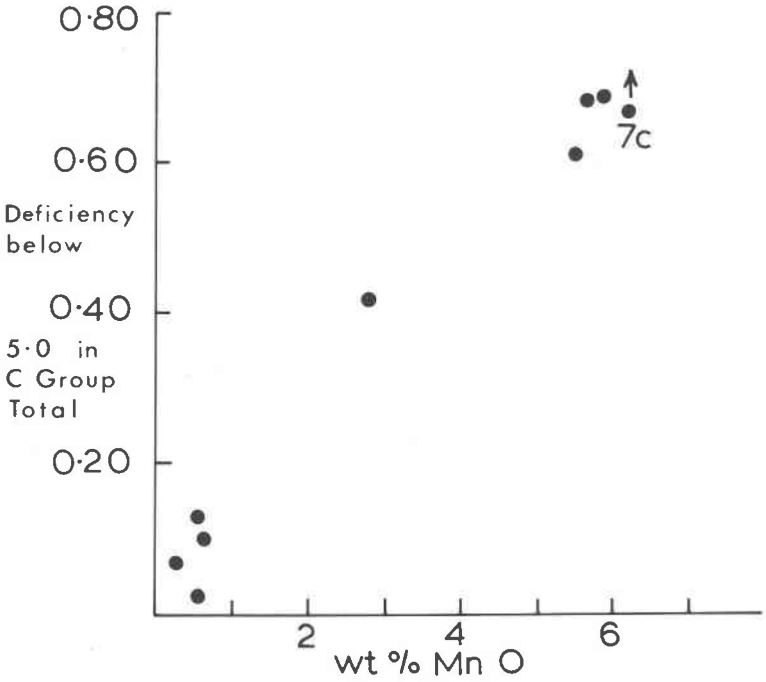

Fig. 2. Plot of Mn contents of amphiboles against the deficiency below 5.00 in the C-group total, *i.e.*, 5.00 minus C-group total.

therefore lower true Ca), and the Si + Al only totals 7.90. Analysis 73 (Leake, 1968) has Si 7.70, Al^{IV} 0.18, Ca 1.11 Na_B 0.78, K 0.21; however, a Si + Al total of 7.88, a C-group total of 5.44, rather low Na and high Ca all indicate an unsatisfactory analysis for the present purpose.

The nearest published analysis to the winchite end-member we know is in Hermes (1973), being a microprobe analysis of a winchite veinlet crossing hornblende in an amphibolite with albite, lawsonite, stilpnomelane, and sphene from the Franciscan blueschist terrain at Panoche Pass, California. On the basis of 23 oxygens, its cation contents are Si = 7.93, $Al^{IV} = 0.08$, $Al^{VI} = 0.59$, Ti = 0.04, Fe^{2+} (assumed) = 2.09, Mn = 0.04, Mg = 2.36, Ca = 1.08, Na = 0.98 and K = 0.01. The A position is therefore only 0.07 filled (*i.e.*, 7%). With Mg/(Mg + Fe) of 0.53, the amphibole should be termed winchite rather than ferrowinchite. The recently published (Wylie and Huggins, 1980) potassian winchite asbestos analysis with Si 7.99, Al^{IV} 0.01, AL^{VI} 0.11, Ti 0.00, Mg 5.02, Fe^{3+} 0.11, Ca 0.68, Na 1.14, K 0.43 is distinguished by low Ca, considerable occupancy of the A position (25% if the excess above 5.00 in the C-group is not carried into B, 45% if it is) and an asbestiform habit probably reflecting a special structure.

As both calcic amphiboles and alkali amphiboles are common in metabasites in appropriate metamorphic terrains, the scarcity of winchite is clearly not due to the scarcity of suitable rock compositions but results from the instability of an amphibole of winchite composition during normal metamorphic P–T conditions. This suggests, but does not prove, that an immiscibility gap exists under natural conditions between tremolite–actinolite–hornblende and glaucophane–crossite–riebeckite.

Acknowledgments

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References

Fermor, L. L. (1904) A new form of blue amphibole from Central India. Records of the Geological Survey of India, 31, 235–236.

Fermor, L. L. (1909) The manganese ore deposits of India. Memoirs of the Geological Survey of India, 37, 1294 pp.

Hermes, O. D. (1973) Paragenetic relationships in an amphibolitic tectonic block in the Franciscan Terrain, Panoche Pass, California. Journal of Petrology, 14, 1–32.

Kemp, A. and Leake, B. E. (1975) Two hydrous-rich aluminous hornblendes. Mineralogical Magazine, 40, 308–311.

Lahiri, D. (1971) Mineralogy and genesis of the manganese oxide and silicate rocks in Kajlidongri and surrounding areas, Jhubua district, Madhya Pradesh, India. Economic Geology, 66, 1176–1185.

Leake, B. E. (1968) A catalog of analyzed calciferous and subcalciferous amphiboles together with their nomenclature and associated minerals. Geological Society of America Special Paper 98.

Leake, B. E. (1978) Nomenclature of amphiboles. American Mineralogist, 63, 1023–1053.

Nayak, V. K. (1962) Studies of manganese silicates from Kajlidongri. Ph.D. Thesis, University of Saugar, India.

Nayak, V. K. and Leake, B. E. (1975) On 'winchite' from the original locality at Kajlidongri, India, Mineralogical Magazine, 40, 395–399.

Wylie, A. G. and Huggins, C. W. (1980) Characteristics of a potassian winchite-asbestos from the Allamoore Talc district, Texas. Canadian Mineralogist, 18, 101–107.

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