American Mineralogist, Volume 58, pages 869–872, 1973

Meteoritic Amphiboles

EDWARD OLSEN

Field Museum of Natural History, Chicago, Illinois 60605, and Department of Geological Sciences, University of Illinois at Chicago Circle, Chicago, Illinois 60680

J. STEPHEN HUEBNER

U.S. Geological Survey, Washington, D.C. 20242

J. A. V. DOUGLAS[1] AND A. G. PLANT

Geological Survey of Canada, Ottawa, Ontario, Canada

Abstract

The crystal chemistry of richterite found in two new meteorite occurrences, as well as that of the original richterite found occurring in a meteorite, is presented. Microprobe chemical analysis indicates that two of the richterites, from the iron meteorites Wichita County and Canyon Diablo, are not fully fluorinated; however, their *a* cell parameters suggest they are fully fluorinated. The cell parameters and the chemical analyses are reconciled by postulating that oxygen ($O^{=}$) substitutes for hydroxyl (OH^{-}) on the O(3)-site. The third richterite, from an enstatite chondrite (Abee), shows *a* and *β* parameters lower than those for fully fluorinated richterite. This is attributed to Mg distributed on the *M*(4)-site, as well as full fluorination, suggesting that a partial solid solution between normal fluorichterite ($NaCaNaMg_5Si_8O_{22}F_2$) and Ca-free fluorichterite ($NaMgNaMg_5Si_8O_{22}F_2$) may exist in nature. There is no evidence for structural water in any of these meteoritic amphiboles.

Introduction

The first noted occurrence of an amphibole of extraterrestrial origin was in the coarse octahedrite iron meteorite, Wichita County (Olsen, 1967). Subsequently, two new occurrences have been found: the coarse octahedrite, Canyon Diablo, and the Type I enstatite chondrite, Abee (Douglas and Plant, 1968). This report will discuss the crystal chemistry of these amphiboles.

The Canyon Diablo occurrence is similar to that described by Olsen for the occurrence in Wichita County. Richterite grains up to a millimeter long are enclosed within a centimeter size graphite inclusion in iron metal; associated minerals are forsterite (Fa 1), krinovite, roedderite, chromite, ureyite, high albite, troilite, and sphalerite.

The occurrence in the Abee meteorite is very different. Abee consists of a breccia of angular fragments set in a fine-grained matrix with metal concentrated along the margins of the fragments. Some podlike segregations of metal occur in the matrix and richterite occurs as clusters of interpenetrating needles (<3.5 mm long) within some of these pods. Enstatite (Fs = O) is also present. Other metal pods lack richterite but contain enstatite, troilite, niningerite, albite, cristobalite, and oldhamite.

Analytical Data

In the original electron microprobe analysis of the Wichita County richterite (Table 1) the fluorine value was determined against the only two available standards at the time, an analyzed hornblende and a synthetic barium fluoride. Both of these were fairly unsatisfactory in terms of their bulk compositions relative to the richterite, although they did give internally consistent fluorine count rates. It was not possible at the time to make accurate mass absorption corrections because of the absence of tables of reliable coefficients for fluorine radiation. Because of the microscopic quantity of richterite, no method of water analysis was applicable, and an amount of water was assumed to be present to satisfy the condition (F + OH) = 2 per amphibole formula unit.

[1] Deceased, June 18, 1971.

TABLE 1. Electron Microprobe Analyses of Three Meteoritic Amphiboles in Wt Percent

	Canyon Diablo*	Abee*	Wichita County*
SiO_2	57.2	57.9	57.8
TiO_2	2.2	0.01	1.5
Al_2O_3	0.38	0.15	0.4
Cr_2O_3	3.5	0.00	0.7
FeO	0.44	0.17	0.5
MnO	0.05	0.00	0.00
MgO	20.9	26.1	22.4
CaO	3.7	5.5	5.8
Na_2O	8.3	7.3	7.5
K_2O	1.2	0.36	0.6
F	3.6	4.6	2.3
Sum	101.5	102.1	99.5
O = F	-1.5	-1.9	-0.9
Total	100.0	100.2	98.6

Cl sought but not detected.

This procedure resulted in OH = 1.0 mole per amphibole formula unit and H_2O = 1.1 wt percent in the analysis.

In an attempt to find a more suitable microprobe standard for fluorine, we used two Na-fluorichterites synthesized by Huebner and Papike (1970). Unfortunately, by this time all of the richterite from Wichita County had been expended due to research requests from other investigators. The original richterite grains were so small that they were lost in the process of repolishing the original probe mount. The richterite from Canyon Diablo was analyzed by microprobe and found to be similar to the Wichita County specimen except for slightly higher K and much higher Cr (balanced by lower Ca and Mg). The fluorine analysis, against the synthetic standard, was repeated in two different laboratories by two different persons with identical results. A single fluorine analysis was made for the Abee sample.

Although the precision of these microprobe analyses is within five relative percent in the original count rate variations, the accuracy is not generally that good. For some elements (Fe, Mn, Ti, Cr, Ca, K) the accuracy may be as good as two percent, assuming we know the compositions of our standards exactly. For other elements (Si, Al, Mg, Na, F) the accuracy is certainly within ten relative percent. In calculating structural formulae (see below) three decimal places were carried for consistency; however, the accuracy is such that no conclusions can be drawn about underpopulations of tetrahedral sites, or under-and-overpopulations of *A*-sites (Table 2). In addition, Table 2 is presented in the standard style of Deer, Howie, and Zussman (1962). This format cascades errors into the *A*-site.

Structural Formulae and Lattice Parameters

The richterite analyses were first recalculated on the basis of 46 negative charges, assuming O = 22 and OH + F = 2 (Table 2). Iron, chromium, and titanium were assumed to be present as Fe^{2+}, Cr^{3+}, and Ti^{4+}, and distributed among the cation sites (Table 2). Next, fluorine was added to the O(3) position, and the formula then could be adjusted in any of four ways. 1) Assume the fluorine analysis is correct, OH is present, and that all 24 anionic sites are filled. Enough water is then added to fluorine to fill the O(3) site (F + OH = 2). 2) Assume that the fluorine analysis is correct, that no hydrogen is present, and that there are still 46 positive and negative charges per formula unit. This distribution results in oxygen vacancies within the structure (not necessarily restricted to O(3)), a highly unlikely situation. 3) Assume the fluorine analysis is incorrect and that no hydrogen is present; fill the O(3) site with 2F (balancing the charge of one of the 23 oxygens in the original formula unit). 4) Assume that the fluorine analysis is correct, that there is no structural hydrogen, and that there are no anionic vacancies. In this case, oxygen substitutes on the O(3) site, and there are more than 46 negative charges per formula unit. The cationic formula is recalculated to preserve electroneutrality. Note that there are two ways to calculate the formula of oxygen-substituted amphibole. In the first method, charge balance is achieved by increasing the assigned valence of various cations; the only possible cation here is Fe^{2+}, which is present in such a small quantity that charge balance cannot be achieved by converting all iron to Fe^{3+}. The other possibility is to increase the number of cations relative to 24 anions. However, the number of cations in any site as given by the idealized structural formula, $A(M4)_2(M(1\text{–}3))_5X_8O_{22}(O, OH, F)_2$, should not be exceeded by more than the analytical uncertainty.

Huebner and Papike (1970) present cell parameters for the substitution of F for OH in richterite and suggest that the Wichita County richterite is fully fluorinated. The cell parameter *a* (or $a \cdot \sin \beta$) is sensitive to this substitution (as well as to the substitution of K for Na). Fixed indexing of Olsen's

(1967) Wichita County richterite X-ray powder diffraction pattern yields the parameters given in Table 3 (Huebner and Papike, 1970). In addition, single crystals of the Wichita County richterite were measured directly by Dr. M. Cameron (personal communication) with the cell dimensions also given in Table 3. When these are compared to the cell parameters (especially a and $a \cdot sin\ \beta$) of synthetic Na-fluorichterite (Huebner and Papike, 1970), it would appear that the Wichita County richterite is indeed fully fluorinated.

Similarly cell parameters obtained for the Canyon Diablo richterite (from fixed indexing of the powder pattern) indicate it too is fully fluorinated. The cell parameters of the Abee specimen indicate full fluorination as well as other peculiarities to be discussed below.

The Abee richterite shows full stoichiometric fluorine (F = 2 moles/formula unit). However, the Canyon Diablo and Wichita specimens show $F < 2$ and must thus have significant OH^- or $O^=$ content in O(3).

The microprobe chemical analyses for fluorine may be reconciled with the richterite cell parameters by a combination of factors. Most important, the substitution of either F^- or $O^=$ for OH^- on the O(3) site would be expected to decrease a and $a \cdot sin\ \beta$, largely due to the removal of the proton[2] associated with O(3). We would expect little change in a or $a \cdot sin\ \beta$ as $F^- \rightleftharpoons O^=$, because hydrogen is not involved. Such substitutions would not change b or c appreciably.

The values a and $a \cdot sin\ \beta$ of an amphibole will be changed to a lesser extent as minor cation substitutions and reorderings are made among the M sites and between the $M(4)$ and A sites. These changes will also affect b and c.

The Abee richterite presents some interesting and unique features. Repeated analyses consistently show more than 5 Mg per formula unit (Tables 1 and 2). In computing the structural formula, it was necessary to insert some of this surplus Mg into $M(4)$ as well as a small amount of the slightly larger Fe ion. If this is actually the case, then this would strongly affect the a parameter (by about 5%). This fact, coupled with full stoichiometric fluorine content, accounts for the fact that both a and β are the smallest values reported for any natural richterite. This is supported by the data of Gibbs, Miller, and Shell (1962) on synthetic Ca-free, Na-Mg fluorichterite where a = 9.677 Å and β = 102°57′. It also suggests at least a partial solid solution (in the probable temperature range of 700°C) between normal fluorichterite ($NaCaNaMg_5Si_8O_{22}F_2$) and Ca-free fluorichterite ($NaMgNaMg_5Si_8O_{22}F_2$).

[2] The hydrogen ion position is such that it tends to push apart the amphibole structure along the a axis; see Huebner and Papike (1970); Papike *et al* (1969).

TABLE 2. Analyses Recalculated to Formula Units

	Canyon Diablo A	Canyon Diablo B	Abee A	Abee B	Wichita County A	Wichita County B
Si	7.884	7.956	7.912	7.914	7.958	8.000
Al	0.062	0.044	0.001	0.001	0.042	--
Ti	0.054	--	0.024	0.024	--	--
Sum	8.000	8.000	7.937	7.939	8.000	8.000
Si	--	--	--	--	--	0.130
Al	--	0.018	--	--	0.023	0.666
Ti	0.174	0.230	--	--	0.155	0.159
Cr	0.382	0.386	--	--	0.076	0.078
Mg	4.293	4.333	5.000	5.000	4.596	4.567
Fe	0.051	0.032	--	--	0.058	--
Mn	0.006	--	--	--	--	--
Ca	0.094	--	--	--	0.092	--
Sum	5.000	5.000	5.000	5.000	5.000	5.000
Mg	--	--	0.316	0.317	--	0.129
Fe	--	0.018	0.019	0.019	--	0.059
Mn	--	0.006	--	--	--	--
Ca	0.452	0.551	0.805	0.805	0.764	0.874
Na	1.548	1.424	0.860	0.859	1.236	0.938
Sum	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.670	0.814	1.074	1.075	0.766	1.107
K	0.211	0.213	0.063	0.063	0.105	0.108
Sum	0.881	1.027	1.137	1.138	0.871	1.215
F	1.569	1.583	1.988	1.988	1.001	1.023
OH	0.431	--	0.012	--	0.999	--
O	--	0.417	--	0.012	--	0.977
Sum	2.000	2.000	2.000	2.000	2.000	2.000
O	22.000	22.000	22.000	22.000	22.000	22.000

A columns: Calculated to 46 positive = 46 negative charges.
B columns: Calculated to O = 24 - F - OH, 24≥O≥22.

Discussion

Evidence for the presence or absence of structural water in extraterrestrial materials has interested

TABLE 3. Unit Cell Data for Richterites

	Wichita County Richterite		Canyon Diablo Richterite	Abee Richterite	Synthetic F-Richterite
a	9.832(6)Å*	9.824(2)Å**	9.812(9)Å	9.767(15)Å	9.838(1)Å***
b	17.954(7)Å	17.955(1)Å	17.924(4)Å	17.966(14)Å	17.963(3)Å
c	5.269(4)Å	5.269(1)Å	5.269(1)Å	5.253(8)Å	5.262(1)Å
β	104°21(3)′	104°11(3)′	104°10(3)′	103°55(7)′	104°15(7)′
$a \cdot sin\ \beta$	9.525(4)Å	9.524Å	9.520(7)Å	9.480Å	9.526(1)Å
V	901.2(7)Å³	901.0(2)Å³	899.1(9)Å³	894.8(±1.6)Å³	900.3(3)Å³

*From Huebner and Papike (1970), refinement of Olsen's (1967) data.
**Independently measured on single crystal by Dr. M. Cameron.
***From Huebner and Papike (1970).

numerous investigators, most recently those working on the lunar samples. Extraterrestrial amphiboles are an excellent potential water barometer or indicator of the presence or absence of significant H_2O in the environment in which the amphibole formed. In the case of the three meteoritic richterites, we find no compelling evidence for the presence of structural water in the amphibole, and thus in the environment in which the amphibole last equilibrated. We would like to caution future investigators against assuming that incomplete fluorination indicates hydroxylation of amphibole.

We expect that additional richterite occurrences will be found as more enstatite chondrites are examined in detail. It is also clear from an ongoing study of silicates in iron meteorites that many of Wasson's Group I irons will contain richterites (Wasson, 1970). Occurrences of richterite in these primitive meteorites (compared to the Earth's crust and mantle) will have implications on fractionation in the Earth and the initial storage of alkalies (especially K) and volatiles (especially water) in the early mantle. Early mantle conditions could be studied by examining the high pressure breakdown products of OH-bearing richterite under water deficient conditions (as has been done for common amphiboles by Wyllie, 1971a, b) as well as under the excess water conditions examined already by Forbes (1971) and Charles (1972).

Acknowledgments

We would like to acknowledge Drs. Kurt Fredericksson (Smithsonian Institution) for performing an independent fluorine analysis, Maryellen Cameron (SUNY/Stony Brook) for her cell measurements of the Wichita County richterite, and Louis Fuchs (Argonne National Laboratory) for his X-ray pattern of the Canyon Diablo richterite. One of us (EO) was supported by a grant from the National Aeronautics and Space Administration, and this is gratefully acknowledged. Drs. Malcolm Ross and David R. Wones, U.S. Geological Survey, provided helpful reviews of the manuscript.

References

CHARLES, R. (1972) *The physical properties and phase equilibria of the hydrous Mg-Fe richterites.* Ph.D. thesis, Massachusetts Institute of Technology, 157 pp.

DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock Forming Minerals.* Longmans, London.

DOUGLAS, J. A. V., AND A. G. PLANT (1968) Amphibole: first occurrence in an enstatite chondrite (abstr.) *Meteoritics,* **4,** 166.

FORBES, W. C. (1971) Synthesis and stability relations of richterite, $Na_2CaMg_5Si_8O_{22}(OH)$. *Amer. Mineral.* **56,** 997–1004.

GIBBS, G. V., J. L. MILLER, AND H. R. SHELL (1962) Synthetic fluormagnesio-richterite. *Amer. Mineral.* **47,** 75–82.

HUEBNER, J. S., AND J. J. PAPIKE (1970) Synthesis and crystal chemistry of sodium-potassium richterite (Na,K) $NaCaMg_5Si_8O_{22}(OH,F)_2$: A model for amphiboles. *Amer. Mineral.* **55,** 1973–1992.

PAPIKE, J. J., M. ROSS, AND J. R. CLARK (1969) Crystal chemical characterization of clinoamphiboles based on five new structure refinements. *Mineral. Soc. Amer. Spec. Pap.* **2,** 117–136.

OLSEN, EDWARD (1967) Amphibole: first occurrence in a meteorite. *Science,* **156,** 61–62.

WASSON, JOHN T. (1970) The chemical classification of iron meteorites. IV. Irons with Ge concentrations greater than 190 ppm and other meteorites associated with Group I. *Icarus,* **12,** 407–423.

WYLLIE, P. J. (1971a) Experimental limits for melting in the Earth's crust and upper mantle. *Amer. Geophys. Union, Geophys. Monograph Ser. V,* **14,** 279–301.

——— (1971b) Role of water in magma generation and initiation of diapiric uprise in the mantle. *Jour. Geophys. Res.* **76,** 1328–1338.

Manuscript received, November 15, 1972; accepted for publication, March 14, 1973.