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THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES. IX. POLYVALENT-CATION ORDERING IN CLINOAMPHIBOLES

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ABSTRACT

The root-mean-square deviation from Pauling's neutrality principle has been calculated for all possible charge arrangements of the twelve common clinoamphibole stoichiometries. In most cases, the arrangement showing the smallest R.M.S. deviation for a specific stoichiometry is insensitive to the coordination numbers assigned to the cations in sites $M(4)$ and A and agrees with the ordering schemes in natural analogues examined by X-ray diffraction. This confirms previous suggestions that local bond-strength requirements are the dominant control on cation ordering in amphiboles. Bond-strength calculations of this sort may be helpful in predicting site occupancies for specific stoichiometries of interest

SOMMAIRE

L'écart (racine du carré moyen) de la règle de neutralité de Pauling a été calculé pour chaque disposition possible des charges dans les douze compositions communes de clinoamphibole. Dans la plupart des cas, la disposition qui montre l'écart le plus petit pour une stoechiométrie donnée n'est pas fonction de la coordination du cation dans les positions $M(4)$ et A, et rappelle le type de mise en ordre que montrent les minéraux analogues étudiés par diffraction X. Ceci confirme l'hypothèse que ce sont surtout les exigences locales quant aux forces de liaison qui gouvernent la mise en ordre des cations dans les amphiboles. De tels calculs des forces de liaison peuvent être utiles pour prédire l'occupation des sites dans certaines compositions stoechiométriques.

(Traduit par la Rédaction)

INTRODUCTION

Polyvalent-cation substitutions (*e.g.*, $2M^{2+} \leftrightarrow M^{3+} + M^{+}$) are extremely common in the amphiboles and account for much of the crystal-chemical complexity of this group of minerals. Several schemes of amphibole classification have been derived based on the various charge-balanced substitutions in amphiboles (Smith 1959, Phillips 1966, Phillips & Layton 1964); Whittaker showed that these various schemes are in fact equivalent, and that a more rational scheme could be derived (Whittaker 1968) which allowed systematic derivation of all possible amphibole types. Of the thirteen integral points in this symmetrical coordinate system, eleven correspond to named amphibole species. Ignoring isovalent substitutions in the amphibole structure, this encompasses virtually all the known amphibole types. Experimental studies have shown that considerable ordering is present in most amphibole species; knowledge of the factor(s) controlling this ordering is pertinent to an understanding of (1) specific amphibole structures and (2) the structural restrictions on variation in chemical composition.

PREVIOUS WORK

In a refinement of the crystal structure of crocidolite, Whittaker (1949) found that the monovalent cations were ordered in $M(4)$ and the trivalent cations were ordered in $M(2)$. The preferential occupancy of $M(2)$ by trivalent cations was explained as arising from the lower electrostatic potential at $M(2)$ that results from the occupancy of the adjacent $M(4)$ position by a monovalent cation. This criterion was also cited by Ghose (1965) as important in controlling cation ordering at the M sites in amphiboles; Ghose also indicated local charge-balance as one of the factors controlling Al/Si ordering in amphiboles with occupied A sites. The effect of the relative electrostatic potential at different sites on polyvalent cation ordering has been considered in more detail by Whittaker (1971). He calculated the Madelung energies and electrostatic site-potentials in a variety of cation arrangements and showed that the results were compatible with the cation arrangements in glaucophane, riebeckite and pargasite (Kakanui hornblende: Papike & Clark 1967). However, the ordering patterns forecast for tschermakite and hornblende do not agree with those subsequently observed in crystal-structure studies (Hawthorne & Grundy 1973, Litvin *et al.* 1972).

A BOND-STRENGTH APPROACH TO ORDERING

In recent years, the importance of local charge neutrality and its effect on bond-length variations in inorganic structures has become apparent (Baur 1961, 1970, 1971; Donnay & Allmann 1970, Evans 1960, Brown & Shannon 1973, Pyatenko 1973, Ferguson 1974). Local charge-neutrality (bond-strength) requirements should also exert stringent controls on polyvalent cation ordering. This approach was considered by Whittaker (1971) who suggested some difficulties encountered with this method. Specifically, it is difficult to apply to the amphibole structure because of uncertainty concerning the coordination number of the $M(4)$ cation, making an unambiguous assignment of bond strengths rather difficult. The same argument also applies to the A cation. Although this factor complicates this type of approach, it no longer constitutes an insuperable difficulty as the coordination number of $M(4)$ is well established for most amphiboles.

TABLE 1. AMPHIBOLE STOICHIOMETRIES EXAMINED IN THIS STUDY

	□	1^+	2^+	3^+	4^+
Tremolite	1	-	7	-	8
Winchite	1	1	5	1	8
Glaucophane	1	2	3	2	8
Richterite	-	2	6	-	8
Arfvedsonite	-	3	4	1	8
Hornblende	1	-	6	2	7
Edenite	-	1	7	1	7
Kataphorite	-	2	5	2	7
Tschermakite	1	-	5	4	6
Pargasite	-	1	6	3	6
Taramite	-	2	4	4	6
Subsilicic pargasite	-	1	5	5	5

TABLE 2. CATION ORDERING PATTERNS SHOWING BEST AGREEMENT WITH PAULING'S NEUTRALITY PRINCIPLE FOR AMPHIBOLES WITH NO TETRAHEDRAL ALUMINUM

Charge arrangement							R.M.S. deviation*			
A	*M*(1)	*M*(2)	*M*(3)	*M*(4)	*T*(1)	*T*(2)	[8]	[10]	[10]	[12]
Winchite										
0.0	2.0	2.5	2.0	1.5	4.0	4.0		10.0		
0.0	1.5	2.5	2.0	2.0	4.0	4.0		11.2		
0.0	2.0	2.5	1.0	2.0	4.0	4.0		11.2		
0.0	2.0	2.0	2.0	2.0	4.0	4.0		11.7		
Glaucophane										
0.0	2.0	3.0	2.0	1.0	4.0	4.0		9.2		
0.0	2.0	3.0	1.0	1.5	4.0	4.0		9.7		
0.0	2.5	2.5	1.0	1.5	4.0	4.0		9.7		
0.0	1.5	3.0	2.0	1.5	4.0	4.0		9.9		
Richterite										
1.0	2.0	2.0	2.0	1.5	4.0	4.0	13.2	13.0	13.2	13.1
0.0	1.5	2.0	2.0	2.0	4.0	4.0	14.6	14.4	14.6	14.4
0.0	2.0	2.0	1.0	2.0	4.0	4.0	14.6	14.4	14.6	14.4
1.0	2.0	1.5	2.0	2.0	4.0	4.0	14.9	14.7	14.9	14.7
Arfvedsonite										
1.0	2.0	2.5	2.0	1.0	4.0	4.0	11.9	11.7	11.9	11.8
1.0	2.0	2.5	1.0	1.5	4.0	4.0	12.8	12.6	12.8	12.6
1.0	1.5	2.5	2.0	1.5	4.0	4.0	12.9	12.8	13.0	12.8
1.0	2.5	2.0	1.0	1.5	4.0	4.0	13.1	12.9	13.1	12.9

* Columns are for different *A*-site coordination numbers.

The occurrence of one specific charge-distribution around a particular anion together with the known stoichiometry imposes restrictions on ordering in other cation sites and produces bond-strength changes around other anions. Thus the charge-distribution pattern must be examined in its entirety rather than simply in restricted parts of the structure. Pauling (1960) defines bond strength between a cation and an anion as the formal cationic charge divided by the number of anions coordinating the cation. Pauling's neutrality principle states that the sum of the bond strengths around an anion is approximately equal to the magnitude of the formal valence of that anion. Thus, the charge distribution over the whole structure may be

TABLE 3. CATION ORDERING PATTERNS SHOWING BEST AGREEMENT WITH PAULING'S NEUTRALITY PRINCIPLE FOR AMPHIBOLES WITH TETRAHEDRAL ALUMINUM

Charge arrangement							R.M.S. deviation*			
A	*M*(1)	*M*(2)	*M*(3)	*M*(4)	*T*(1)	*T*(2)	[8]	[10]	[10]	[12]
Hornblende										
0.0	2.0	2.5	2.0	2.0	3.75	4.00		8.9		
0.0	2.0	2.5	2.0	2.0	4.00	3.75		10.0		
0.0	2.0	2.0	2.0	2.5	3.75	4.00		10.5		
0.0	2.0	2.0	2.0	2.5	4.00	3.75		11.3		
Edenite										
1.0	2.0	2.0	2.0	2.0	3.75	4.00	12.0	11.8	12.1	11.8
1.0	2.0	2.0	2.0	2.0	4.00	3.75	13.2	13.0	13.3	13.1
2.0	2.0	2.0	2.0	1.5	3.75	4.00	13.9	13.5	14.0	13.6
2.0	2.0	2.0	2.0	1.5	4.00	3.75	15.4	15.0	15.4	15.3
Kataphorite										
1.0	2.0	2.5	2.0	1.5	3.75	4.00	10.4	10.3	10.5	10.2
1.0	2.0	2.5	2.0	1.5	4.00	3.75	11.9	11.7	11.9	11.8
1.0	1.5	2.5	2.0	2.0	3.75	4.00	11.0	11.7	12.0	11.6
1.0	2.0	2.0	2.0	2.0	3.75	4.00	12.0	11.8	12.1	11.8
Tschermakite										
0.0	2.0	3.0	2.0	2.0	3.50	4.00		7.5		
0.0	2.0	3.0	2.0	2.0	3.75	3.75		7.9		
0.0	2.0	2.5	2.0	2.5	3.50	4.00		8.7		
0.0	2.0	2.5	2.0	2.5	3.75	3.75		8.9		
Pargasite										
1.0	2.0	2.5	2.0	2.0	3.50	4.00	9.5	9.5	9.7	9.2
1.0	2.0	2.5	2.0	2.0	3.75	3.75	10.4	10.3	10.5	10.2
2.0	2.0	2.5	2.0	1.5	3.50	4.00	11.1	10.8	11.2	10.6
1.0	2.0	2.0	2.0	2.5	3.50	4.00	11.4	11.3	11.5	11.0
Taramite										
1.0	2.0	3.0	2.0	1.5	3.50	4.00	8.1	8.1	8.3	7.8
1.0	2.0	3.0	2.0	1.5	3.75	3.75	9.2	9.1	9.3	9.1
2.0	2.0	3.0	2.0	1.0	3.50	4.00	9.6	9.3	9.7	9.2
1.0	2.0	2.5	2.0	2.0	3.50	4.00	9.5	9.5	9.7	9.2
Subsilicic pargasite										
1.0	2.0	3.0	2.0	2.0	3.25	4.00	8.0	8.0	8.2	7.5
1.0	2.0	3.0	2.0	2.0	3.50	3.75	8.1	8.1	8.3	7.8
2.0	2.0	3.0	2.0	1.5	3.25	4.00	8.8	8.6	9.0	8.0
1.0	2.0	2.5	2.0	2.5	3.25	4.00	9.2	9.1	9.7	9.1

* Columns are for different *A*-site coordination numbers.

assessed by its root-mean-square (R.M.S.) deviation from exact agreement with Pauling's neutrality principle. The percent root-mean-square deviation of anion bond-strength sums per unit cell is given by:

$$100\sqrt{\left[\left(\sum_{i=1}^{n} m_i\,(\Delta\, s_i/z_i)^2\right) \Big/ \sum_{i=1}^{n} m_i\right]}$$

In this expression of % deviation, s_i is bond-strength sum to the ith anion, z_i is the valence of ith anion, $\Delta s_i = z_i - s_i$, m_i is the multiplicity of the equipoint occupied by the ith anion, and n is the number of crystallographically unique anions. Possible ordering schemes may be examined by carrying out this procedure for all possible cation arrangements with a specific stoichiometry.

Coordination of the M(4) cation

Examination of empirical bond-strength tables for clinoamphiboles (Hawthorne 1978), calculated using the bond-strength curves of Brown & Shannon (1973), shows that in all except possibly the ferromagnesian amphiboles,

TABLE 4. COMPARISON OF CLINOAMPHIBOLE SITE-POPULATIONS FORECAST FROM A BOND-STRENGTH CRITERION WITH THOSE OBSERVED IN CRYSTAL-STRUCTURE REFINEMENTS

	A	M(1)	M(2)	M(3)	M(4)	T(1)	T(2)	Reference
TREMOLITE	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	
Tremolite	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.06M^{+}+0.94M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	(1)
Fluor-tremolite	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	(2)
Tremolite	$0.30M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.10M^{+}+0.90M^{2+}$	$0.05M^{3+}+0.95M^{4+}$	$0.01M^{3+}+0.99M^{4+}$	(3)
Actinolite	$0.30M^{+}$	$1.0M^{2+}$	$0.84M^{2+}+0.16M^{3+}$	$1.0M^{2+}$	$0.04M^{+}+0.96M^{2+}$	$0.07M^{3+}+0.93M^{4+}$	$0.01M^{3+}+0.99M^{4+}$	(4)
PARGASITE	$1.0M^{+}$	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$	
Pargasite	$0.93M^{+}$	$1.0M^{2+}$	$0.48M^{2+}+0.52M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.44M^{3+}+0.56M^{4+}$	$0.03M^{3+}+0.97M^{4+}$	(5)
Titanian pargasite	$0.79M^{+}$	$1.0M^{2+}$	$0.44M^{2+}+0.56M^{3+}$	$1.0M^{2+}$	$0.08M^{+}+0.92M^{2+}$	$0.47M^{3+}+0.53M^{4+}$	$0.07M^{3+}+0.93M^{4+}$	(5)
Kakanui Hornblende	$1.0M^{+}$	$1.0M^{2+}$	$0.45M^{2+}+0.55M^{3+}$	$1.0M^{2+}$	$0.11M^{+}+0.89M^{2+}$	$0.42M^{3+}+0.58M^{4+}$	$0.08M^{3+}+0.92M^{4+}$	(5)
EDENITE*	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.25M^{3+}+0.75M^{4+}$	$1.0M^{4+}$	
GLAUCOPHANE	-	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$1.0M^{+}$	$1.0M^{4+}$	$1.0M^{4+}$	
Glaucophane	-	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$0.98M^{+}+ 0.02M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	(6)
RICHTERITE	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	
Richterite (001)	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.50M^{+}+0.50M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	(7)
Richterite (002)	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.49M^{+}+0.51M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	(7)
Potassium richterite	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.50M^{+}+0.50M^{2+}$	$0.06M^{3+}+0.94M^{4+}$	$0.01M^{3+}+0.99M^{4+}$	(7)
ARFVEDSONITE	$1.0M^{+}$	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$1.0M^{+}$	$1.0M^{4+}$	$1.0M^{4+}$	
Potassium arfvedsonite	$1.0M^{+}$	$1.0M^{2+}$	$0.42M^{2+}+0.58M^{3+}$	$1.0M^{2+}$	$0.92M^{+}+0.08M^{2+}$	$0.04M^{3+}+0.96M^{4+}$	$1.0M^{4+}$	(8)
TSCHERMAKITE	-	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$	
Ferro-tschermakite	$0.23M^{+}$	$1.0M^{2+}$	$0.10M^{2+}+0.90M^{3+}$	$1.0M^{2+}$	$0.05M^{+}+0.95M^{2+}$	$0.44M^{3+}+0.56M^{4+}$	$0.06M^{3+}+0.94M^{4+}$	(9)
HORNBLENDE	-	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.25M^{3+}+0.75M^{4+}$	$1.0M^{4+}$	
Magnesio-hornblende	$0.18M^{+}$	$1.0M^{2+}$	$0.35M^{2+}+0.65M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.24M^{3+}+0.76M^{4+}$	$0.06M^{3+}+0.94M^{4+}$	(10)
TARAMITE	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$	
Potassium ferri-taramite	$0.97M^{+}$	$1.0M^{2+}$	$0.21M^{2+}+0.79M^{3+}$	$1.0M^{2+}$	$0.37M^{+}+0.63M^{2+}$	$0.43M^{3+}+0.57M^{4+}$	$0.03M^{3+}+0.97M^{4+}$	(11)
KATAPHORITE*	$1.0M^{+}$	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$0.25M^{3+}+0.75M^{4+}$	$1.0M^{4+}$	
WINCHITE**	-	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$	
SUBSILICIC PARGASITE	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.75M^{3+}+0.25M^{4+}$	$1.0M^{4+}$	
Subsilicic Hastingsite***	$1.0M^{+}$	$1.0M^{2+}$	$0.21M^{2+}+0.79M^{3+}$	$1.0M^{2+}$	$0.06M^{+}+0.94M^{2+}$	$0.49M^{3+}+0.51M^{4+}$	$0.19M^{3+}+0.81M^{4+}$	(12)

References: (1) Papike et al. (1969): (2) Cameron & Gibbs (1973): (3) Hawthorne & Grundy (1976): (4) Mitchell et al. (1971): (5) Robinson et al. (1973): (6) Papike & Clark (1968): (7) Cameron & Gibbs (1971): (8) Hawthorne (1976): (9) Hawthorne & Grundy (1973): (10) Litvin et al. (1972): (11) Hawthorne & Grundy (1978): (12) Hawthorne & Grundy (1977b).

*Data not at present available for these structures. **Preliminary results (Hawthorne, in prog.) appear to confirm this ordering pattern. ***A small amount of ferric iron (0.19 atoms p.f.u.) occurs at M(1) and/or M(3).

the $M(4)$ coordination number is eight. The relative strengths of the $M(4)$–O bonds vary considerably, but in all cases where $M(4)$ is occupied by Ca or Na, or both, all eight bonds appear to contribute significantly to the bond-strength sums around the anions. The coordination number of the $M(4)$ cation in the ferromagnesian amphiboles is considered in detail by Hawthorne & Grundy (1977a). Although the evidence was not considered completely conclusive, they suggested that fourfold coordination of $M(4)$ in the cummingtonites was not correct, and that the coordination number was either six or eight.

Coordination of the A cation

This aspect of the clinoamphibole structures has been examined by Hawthorne & Grundy (1978). They concluded that (i) where the A-site cation is K, it occupies the $A(m)$ position with a coordination number of [8]; (ii) where the A-site cation is Na, it occupies the $A(2)$ or $A(1)$ position with possible coordination numbers [10] and [12].

In the present study, the coordination numbers: [8], [10] (4xO(5), 3xO(6), 3xO(7)), [10] (4xO(5), 4xO(6), 2xO(7)) and [12] were considered.

DISCUSSION

Calculations were performed for all twelve stoichiometries indicated in Table 1 and the results are given in Tables 2 and 3. In Table 4, a comparison is made between the ordering patterns showing the smallest R.M.S. deviation from Pauling's neutrality principle for the stoichiometries of Table 1 with the site-ordering patterns derived from crystal-structure refinements. In some cases, complete site-population data were not given by the original author(s); in these cases, site populations were derived for this study from the mean bond-length–ionic-radius relationships given by Hawthorne & Grundy (1977b) and Hawthorne (1978). With the exception of subsilicic hastingsite, all ten stoichiometric types of clinoamphiboles thus far refined show ordering patterns that agree with the ordering patterns showing the smallest R.M.S. deviation from Pauling's neutrality principle. This indicates that local bond-strength requirements play a dominant role in controlling polyvalent cation ordering in clinoamphiboles. This being the case, bond-strength calculations of this sort may be helpful in forecasting cation-ordering patterns in other stoichiometric variants.

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