

EVALUATION OF TETRAHEDRAL Al IN TRIOCTAHEDRAL CHLORITES FROM b AND d_{001} DATA

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Abstract: Analysis of structural and chemical data on trioctahedral chlorites has yielded a relationship that allows estimating the amount of tetrahedral Al up to 0.14 at. per $O_{10}(OH)_8$ from the data on b and d_{001} parameters.

Key words: trioctahedral chlorite, Al for Si substitution, XRD powder data.

In our recent paper (Drits & Smoliar-Zviagina 1992) we analysed the interrelationships between structural parameters and chemical compositions of trioctahedral chlorites and concluded that the complicated pattern in the dependence of d_{001} on cation composition hampers direct estimation of chlorite composition from d_{001} data. The problem, however, can be simplified if we make use of a peculiarity characteristic of trioctahedral chlorite structures that was not taken into account in the previous paper. Careful analysis of high-precision chlorite structural data has shown that the mean interatomic cation-anion distance in the brucite-like layer (d_{br}) is related by a constant factor to the b parameter:

$$b/d_{br} = 4.528 \pm 0.007 \quad (1)$$

Owing to greater distortions of the octahedra this rule is not as strictly obeyed as in the case of the 2 : 1 layer (Drits & Smoliar-Zviagina 1992):

$$b/d_{oct} = 4.440 \pm 0.004 \quad (2)$$

but allows, nevertheless, the amount of tetrahedral aluminum, Al_t (in atoms per $O_{10}(OH)_8$), to be expressed in terms of b and d_{001} parameters. This is done as follows.

Equations (1) and (2) are combined with the formulae for the tetrahedral sheet thickness h_t the distance separating the 2 : 1 layer and the brucite-like layer h_{sep} the octahedral sheet thickness calculated from the non-hydroxyl oxygens, $h_{oct,max}$, and the brucite-like layer thickness, h_{br} :

$$h_t = (l_p^2 - l_b^2/3)^{1/2} \quad (3)$$

where l_p and l_b are tetrahedral apical and basal edgelengths, respectively, given by

$$l_b = 1.623d_t$$

$$l_p = 3.266d_t - l_b$$

and $d_t = 1.616 + 0.0375 Al_t$ is the mean tetrahedral bondlength (Eqs. 6 - 9, Drits & Smoliar-Zviagina 1992);

$$h_{sep} = 2.847 - 0.042(Al_t)^3 \quad (4)$$

$$h_{oct,max} = 1.038d_{oct} + 0.034 \quad (5)$$

$$h_{br} = 0.978d_{br} \quad (6)$$

(Eqs. 11-14, Drits & Smoliar-Zviagina 1992). Combination of (1-6) with the formula

$$d_{001} = h_{oct,max} + h_{br} + 2(h_t + h_{sep})$$

gives

$$(Al_t)^3 - 1.214Al_t + 11.905d_{001} - 5.355b - 120.119 = 0 \quad (7)$$

It can be shown that (7) has a unique, crystal-chemically reasonable solution if

$$d_{001} - 0.4498b = 10.133 \text{ or } d_{001} - 0.4498b \leq 10.090;$$

which corresponds to $Al_t \geq 1.102$ at. per $O_{10}(OH)_8$.

If $10.090 < d_{001} - 0.4498b < 10.133$, there are two positive roots, and basing on the supposition of Bailey (1988) that the layer charge in chlorites is most often close to unity, we suggest that the root which is closer to unity should be chosen. Application of (7) to 17 chlorite samples (Nos.1-10, Tab. 1 and 1 - 4, 7 - 9, Tab. 2, Drits & Smoliar-Zviagina 1992) has shown that the standard deviation between the reported and calculated Al_t values is 0.14 at. per $O_{10}(OH)_8$. The experimental and calculated data are compared in Tab. 1.

Thus application of structural considerations has allowed us not only to investigate the factors affecting the dependence of d_{001} on chlorite composition but also to obtain, for the first time, a relatively simple equation for estimating the contents of tetrahedral Al from XRD powder data. Table 2 compares the observed and calculated Al_t and Σ_{tr} (sum of transition-metal octahedral

Table 1: Experimental and calculated Al_t values for trioctahedral chlorites.

No.	Sample*	$(Al_t)_{exp}$	$(Al_t)_{calc}$
1	Penninite IIb-4	0.84	0.65
2	Cr-clinocllore IIb-4 (Day Book Body)	1.01	1.05
3	Cr-clinocllore IIb-4 (Siskiyou Cty)	0.98	1.11
4	Fe-clinocllore IIb-2 (Washington)	1.38	1.37
5	Clinocllore IIb-4 (Kenya)	0.94	1.04
6	Clinocllore IIb-2 (Kenya)	0.94	0.96
7	Clinocllore IIb-4 (Urals)	1.15	1.11
8	Clinocllore IIb-2 (Urals)	1.15	1.16
9	Cr-chlorite Ia-4	0.85	0.68
10	Baileychlore	0.45	0.82
11	Chlorite IIb (N. Hampshire)	1.54	1.61
12	Corundophyllite	0.98	0.93
13	Sayama mine	1.45	1.63
14	22	0.90	0.70
15	257	1.39	1.38
16	271	0.99	1.03
17	296	1.40	1.39

* For references, see Tabs. 1, 4 in Drits & Smoliar-Zviagina 1992.

Table 2: Experimental and calculated Al_t and Σ_{tr} values for chlorites of Prieto et al. (1991).

Sample	b	d_{001}	Al_t		Σ_{tr}	
			exp	calc	exp	calc
P1	9.234	14.33	0.69	0.63	0.25	0.50
P2	9.240	14.17	1.00	1.37	0.44	0.70
P3	9.240	14.15	1.20	1.41	0.43	0.70
P4	9.300	14.15	1.27	1.48	2.25	2.70
B5	9.288	14.10	1.46	1.57	2.08	2.30
P6	9.342	14.12	1.40	1.58	4.19	4.10
B7	9.342	14.11	1.29	1.60	4.33	4.10
B8	9.328	14.12	1.50	1.57	3.48	3.63

cations) values for several chlorites (Prieto et al. 1991) that have not been part of the initial data set (Σ_{tr} values have been calculated from the equation $b = 9.219 + 0.030 \Sigma_{tr}$, Drits & Smoliar-Zviagina 1992).

In the case of $d_{001} - 0.4498b > 10.133$ Eq. (7) has no positive solutions. The relationship between b and d_{001} may therefore lead to inferences on crystal-chemical factors controlling the existence of a chlorite structure of a certain composition. Thus the relationships obtained allow estimating, at least to the first approximation, the compositions of both tetrahedral and octahedral sheets in chlorite layers from powder XRD data.

References

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