that Na would occupy the M(4) and A sites in the amphibole structure, and this was confirmed experimentally by Whittaker (1949) and Heritsch et al. (1957). All subsequent crystal-structure work has confirmed these results.

Potassium

K is always assigned to the A group in the amphibole formula unit, and all experimental work so far published is in agreement with this (Papike et al. 1969, Cameron et al. 1973b, Hawthorne 1976). The positional disorder of Na and K is discussed in the section on the A site.

Beryllium

Joesmithite is a remarkable amphibole in which Be^{2+} occupies the T(1)B site, apparently showing no disorder with Si over the four distinct tetrahedral sites. The occupancy of a T(1)-type site by Be^{2+} is in accord with the criteria based on local charge-balance proposed by Hawthorne (1978c).

Boron

Kohn & Comeforo (1955) reported the synthesis of a calcic fluor-amphibole containing considerable B^{3+}. The chemical analysis indicates $1.12^{iv}B$ and $0.33^{vi}B$ p.f.u.; as B^{3+} has not been recorded in octahedral co-ordination in an oxide environment, additonal evidence is needed before this result can be accepted.

Cobalt

Co^{2+} occupies the M(1), M(2), M(3) and M(4) sites in the structure of "$Na_2H_2Co_5Si_8O_{22}(OH)_2$" (Prewitt 1963, Gibbs & Prewitt 1968), which apparently deviates somewhat from its ideal composition. Similar results are apparent from the chemical analysis of fibrous cobalt amphibole synthesized by Nesterchuk et al. (1968). On the basis of optical-absorption spectra, Chigareva et al. (1969) proposed that Co^{2+} occurs in both octahedral and [8]-fold co-ordination in synthetic cobalt fluor-richterite.

Nickel

Chemical analysis of synthetic nickel richterite (Fedoseev et al. 1968, 1970) shows Ni to occupy the M(1), M(2), M(3) and M(4) sites. Absorption spectra of a nickel fluor-richterite suggest the presence of Ni^{2+} in both octahedral and [8]-fold co-ordination (Chigareva et al. 1969).

Chromium

On the basis of optical-absorption spectra,

Chigavera et al. (1969) proposed that Cr^{3+} occurs in [8]-fold co-ordination in "chromium fluor-amphibole".

Zinc

Klein & Ito (1968) reported results of chemical analyses and physical data for several zinc-bearing amphiboles from Franklin, New Jersey. In zincian tirodite, the Zn content may attain 1.22 atoms p.f.u.; a combined X-ray structure refinement and Mössbauer-spectroscopy study (Hawthorne & Grundy 1977b) of zincian tirodite(57) showed the Zn site occupancy M(1) > M(3) ≫ M(2) > M(4). Chemical analyses of zinc-bearing amphiboles of the tremolite – ferro-actinolite series suggest that Zn is strongly ordered at the M(1), M(2) or M(3) sites (or all three) (Klein & Ito 1968); a similar preference appears to be exhibited by zincian magnesio-riebeckite.

Germanium

Sipovskii et al. (1972) and Grebenshchikov et al. (1974) reported synthesis and characterization of a fibrous amphibole, $Na_2Mg_6Ge_8 O_{22}(OH)_2$, where Si is entirely replaced by Ge. As the ionic radius of Ge is slightly larger than that of Si, the cell parameters of the germanate amphibole are all slightly larger than those of the silicate analogue (Table 61).

FACTORS AFFECTING CATION ORDERING IN AMPHIBOLES

The amphibole structures have a wide variety of cation sites that can accept cations in the range 0.26–1.60 Å in size and 1+ to 4+ in formal charge. The extreme diversity of chemistry that this allows, together with the similarity of symmetrically distinct cation polyhedra, ensures that extensive solid-solution will occur

TABLE 61. COMPARISON OF CELL PARAMETERS FOR GERMANATE AND SILICATE AMPHIBOLES*

	$Na_2Mg_6Si_8O_{22}(OH)_2$	$Na_2Mg_6Ge_8O_{22}(OH)_2$
a(Å)	9.70(1)	9.98(1)
b(Å)	18.01(1)	18.31(1)
c(Å)	5.28(2)	5.35(5)
β(°)	103.0(1)	106.5(2)
V(Å³)	900(5)	935(10)
Space group	C2/m	C2/m
	2.98(2)	4.07(5)

*from Grebenshchikov et al. (1974)

with all the possibilities of cation order-disorder relationships. Several studies have examined the factors affecting cation ordering in amphiboles (Ghose 1962, 1965, 1977, Litvin 1966, 1972, Hawthorne 1978c) but as yet the problem is far from being resolved, and there remains much experimental work still to do before an overall view is possible.

Structure energy

In a refinement of the crystal structure of magnesio-riebeckite(3), Whittaker (1949) found that the monovalent cations were ordered at the M(4) site and the trivalent cations were ordered at the M(2) site. 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) site by a monovalent cation. As indicated by Whittaker (1971), this does not completely explain the situation, as the question then arises as to why the monovalent cation occupies the M(4) site. In the case of riebeckite, this may be assumed to result from the large size of the Na atom. However, for holmquistite and clinoholmquistite, which show a similar cation-charge arrangement, this argument cannot apply, as Li is small enough to occupy the M(1), M(2) or M(3) sites, (or all three), and has been shown to do so in Li-bearing riebeckite (Hawthorne 1978b). Ghose (1965) has also cited this factor as affecting cation-ordering in amphiboles and further suggested that Fe^{3+} and Ti^{4+} may occupy the M(1) and M(3) sites in oxy-amphiboles. The effect of relative

electrostatic potentials at different sites in the amphibole structures has been considered in more detail by Whittaker (1971). The total site-potential consists of the electrostatic site-energy, repulsive energy, van der Waals energy and multipole–multipole interaction energy. Whittaker (1971) assumed that the short-range repulsive forces would be approximately independent of the charge arrangement; this being the case, the site-preference energies for ions of different charge are given by the differences in Madelung energies of the appropriate distributions of ions. He further found that the site preferences in charge-balancing substitutions could be predicted qualitatively from the electrostatic potentials at the cation sites in the structure that is regarded as the parent one in the substitution. Table 62 lists some site potentials obtained by Whittaker (1971). From these calculations, which show good qualitative and semiquantitative agreement with the cation-ordering patterns in glaucophane(26), fluor-riebeckite(68) and potassian pargasite(38), the following predictions were made:

(i) Richterite should have Na at A and NaCa at M(4), not Ca at A and Na_2 at M(4); this was confirmed by Cameron & Gibbs (1971) for fluor-richterite(34) and (35).

(ii) Clinoholmquistite should have Li_2 at M(4); this was shown to be the case by Litvin et al. (1975a).

(iii) Lithian fluor-richterite $LiNaMg_6Si_8O_{22}F_2$ should have Na at A, Mg_2 at M(4) and Li at M(3); there is no experimental evidence concerning this species.

TABLE 62. SITE POTENTIALS ($e^2/Å$) IN A FEW CLINOAMPHIBOLE ARRANGEMENTS (AFTER WHITTAKER (1971) EXCEPT WHERE INDICATED)

	M(1)=M(2)=M(3)=M(4)=M^{2+}; T(1)=T(2)=T^{4+}					M(2)=M^{3+}; M(4)=M^+		M(1)=M^{3+}; M(2)=M^+
	OH^1	F^1	OH^2	OH^3	F^3	OH^1	F^1	OH^1
T(1)	-3.233	-3.236	–	-3.341	-3.338	-3.079	-3.079	-3.190
T(2)	-3.230	-3.217	–	-3.328	-3.314	-3.138	-3.215	-3.313
M(1)	-1.726	-1.476	-1.543	-1.905	-1.657	-1.485	-1.233	-2.066
M(2)	-1.776	-1.700	-1.752	-2.163	-2.013	-2.089	-2.013	-1.364
M(3)	-1.719	-1.439	-1.519	-1.903	-1.625	-1.422	-1.143	-1.495
M(4)	-1.508	-1.474	-1.608	-1.385	-1.359	-0.945	-0.911	-1.650
A	-0.246	-0.369	–	-0.313	-0.440	-0.246	-0.249	-0.206
O(1)	1.920	2.052	–	1.726	1.857	2.237	2.369	2.029
O(2)	1.917	1.984	–	1.769	1.839	2.085	2.152	1.853
O(3)	1.877	0.959	–	1.707	0.789	2.118	1.200	2.270
H	-1.504	–	–	-1.657	–	-1.306	–	-1.284
O(4)	1.900	1.934	–	1.817	1.854	1.983	2.017	1.658
O(5)	2.189	2.174	–	2.127	2.112	2.298	2.283	2.131
O(6)	2.213	2.190	–	2.182	2.162	2.269	2.246	2.215
O(7)	2.204	2.151	–	2.129	2.082	2.351	2.298	2.280

[1]calculated using atomic coordinates of cummingtonite(21); [2]calculated using atomic coordinates of grunerite(22) by Minyeva (1973); [3]calculated using atomic coordinates of glaucophane(26)

(iv) Oxy-amphiboles should have a preference for Y^{2+} or Y^{4+} at M(1); Kitamura *et al.* (1975) have shown that Ti preferentially occupies M(1) in potassian oxy-kaersutite(40). However, Hawthorne & Grundy (1973b) argued that local steric constraints could also give rise to this type of ordering.

(v) All amphiboles (except oxy-amphiboles) should have octahedral trivalent cations (Al,Fe^{3+}) strongly ordered at M(2); as indicated in Appendices B3 and C3, this appears to be the case.

(vi) In magnesio-hornblende and tschermakite, T(2) should be preferentially occupied by Al; Litvin *et al.* (1971b) and Hawthorne & Grundy (1973a) have shown that this is not the case, as Al is strongly ordered in T(1) in both these species.

(vii) In edenite, katophorite and taramite, T(1) should be preferentially occupied by Al; there are no data for the first two species, but Hawthorne & Grundy (1978) have confirmed this pattern for potassian ferri-taramite(59).

Mineyeva (1973) has also calculated the site potential at the M sites in grunerite, using the structure of grunerite(22); the values are compared with Whittaker's (1971) values in Table 62.

Bond valence

The effect of local charge-balance around the

TABLE 63. COMPARISON OF CLINOAMPHIBOLE SITE-POPULATIONS FORECAST FROM A BOND-STRENGTH CRITERION WITH THOSE OBSERVED IN CRYSTAL-STRUCTURE REFINEMENT

	A	M(1)	M(2)	M(3)	M(4)	T(1)	T(2)
TREMOLITE	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Tremolite(30)	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.06M^{+}+0.94M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Fluor-tremolite(36)	-	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Tremolite(56)	$0.30M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.10M^{+}+0.90M^{2+}$	$0.05M^{3+}+0.95M^{4+}$	$0.01M^{3+}+0.99M^{4+}$
Manganoan ferro-actinolite(37)	$0.30M^{+}$	$1.0M^{2+}$	$0.84M^{2+}+0.16M^{3+}$	$1.0M^{2+}$	$0.04M^{+}+0.96M^{2+}$	$0.07M^{3+}+0.93M^{4+}$	$0.01M^{3+}+0.99M^{4+}$
PARGASITE	$1.0M^{+}$	$1.0M^{2+}$	$0.5M^{2+}+0.5M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$
Potassian pargasite(38)	$0.93M^{+}$	$1.0M^{2+}$	$0.48M^{2+}+0.52M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.44M^{3+}+0.56M^{4+}$	$0.03M^{3+}+0.97M^{4+}$
Potassian titanian pargasite(39)	$0.79M^{+}$	$1.0M^{2+}$	$0.44M^{2+}+0.56M^{3+}$	$1.0M^{2+}$	$0.08M^{+}+0.92M^{2+}$	$0.47M^{3+}+0.53M^{4+}$	$0.07M^{3+}+0.93M^{4+}$
Potassian titanian magnesio-hastingsite(24)	$1.0M^{+}$	$1.0M^{2+}$	$0.45M^{2+}+0.55M^{3+}$	$1.0M^{2+}$	$0.11M^{+}+0.89M^{2+}$	$0.42M^{3+}+0.58M^{4+}$	$0.08M^{3+}+0.92M^{4+}$
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(26)	-	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$0.98M^{+}+0.02M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
RICHTERITE	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Fluor-richterite(35)	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.50M^{+}+0.50M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Fluor-richterite(36)	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.49M^{+}+0.51M^{2+}$	$1.0M^{4+}$	$1.0M^{4+}$
Potassium-magnesio-kataphorite(29)	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.50M^{+}+0.50M^{2+}$	$0.06M^{3+}+0.94M^{4+}$	$0.01M^{3+}+0.99M^{4+}$
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(67)	$1.0M^{+}$	$1.0M^{2+}$	$0.42M^{2+}+0.58M^{3+}$	$1.0M^{2+}$	$0.92M^{+}+0.08M^{2+}$	$0.04M^{3+}+0.96M^{4+}$	$1.0M^{4+}$
TSCHERMAKITE	-	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$
Ferro-tschermakite(54)	$0.23M^{+}$	$1.0M^{2+}$	$0.10M^{2+}+0.90M^{3+}$	$1.0M^{2+}$	$0.05M^{+}+0.95M^{2+}$	$0.44M^{3+}+0.56M^{4+}$	$0.06M^{3+}+0.94M^{4+}$
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(45)	$0.18M$	$1.0M^{2+}$	$0.35M^{2+}+0.65M^{3+}$	$1.0M^{2+}$	$1.0M^{2+}$	$0.24M^{3+}+0.76M^{4+}$	$0.06M^{3+}+0.094M^{4+}$
TARAMITE	$1.0M^{+}$	$1.0M^{2+}$	$1.0M^{3+}$	$1.0M^{2+}$	$0.5M^{+}+0.5M^{2+}$	$0.5M^{3+}+0.5M^{4+}$	$1.0M^{4+}$
Potassian ferri-taramite(59)	$0.97M^{+}$	$1.0M^{2+}$	$0.21M^{2+}+0.79M^{3+}$	$1.0M^{2+}$	$0.37M^{+}+0.63M^{2+}$	$0.43M^{3+}+0.57M^{4+}$	$0.03M^{3+}+0.97M^{4+}$
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 titanian magnesio-hastingsite(58)***	$1.0M^{+}$	$1.0M^{2+}$	$0.21M^{2+}+0.79M^{3+}$	$1.0M^{2+}$	$0.06M^{+}+0.94M^{2+}$	$0.49M^{3+}+0.51M^{4+}$	$0.19M^{3+}+0.81M^{4+}$

*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)

bridging anions in amphiboles with occupied A-sites has been examined by Ghose (1965), who concluded that tetrahedral Al should order in the T(1) site. Hawthorne (1978c) has considered the effect of local bond-valence requirements on the cation-ordering patterns in amphiboles. Other work (Baur 1961, 1970, 1971, Donnay & Allmann 1970, Evans 1960, Brown & Shannon 1973, Pyatenko 1973, Ferguson 1974) has shown the importance of local bond-valence requirements on the variation of bond lengths, suggesting that the same mechanism should exert stringent controls on cation ordering. Whittaker (1971) considered this approach, but suggested that the occurrence of sites with ambigous co-ordination numbers made this approach rather difficult to apply. However, this proved not to be a problem as the specific method used by Hawthorne (1978c) turned out not to be sensitive to assigned co-ordination-numbers of cations. This involved the calculation of the root-mean-square (R.M.S.) deviation from exact agreement with Pauling's second rule (Pauling 1960) for all possible arrangements of charges consonant with a particular amphibole stoichiometry; the arrangement showing the smallest R.M.S. deviation is the preferred arrangement of cations for that specific stoichiometry. The preferred patterns of ordering for all stoichiometries of interest are shown in Table 63, where they are compared with analogous experimental results. With the exception of subsilicic titanian magnesian hastingsite(58), all stoichiometric types of clinoamphiboles thus far refined show patterns of ordering that agree with those forecast from this bond-strength criterion.

Miscellaneous factors

Although reasonable success has been achieved in the rationalization of cation ordering in amphiboles by energy and bond-strength methods, these methods only apply to the relative ordering of cation species with different formal valences. They do not apply (at least at the present level of sophistication) to $Al-Fe^{3+}$ and $Mg-Fe^{2+}-Mn$ ordering, and an appeal to other criteria must be made. Ghose (1977) has reviewed several factors that may influence ordering in amphiboles:

(i) *ionic size:* Ghose (1965) suggested that this factor plays a role in the site occupancy of the M(4) site. The large [8]-fold site in the monoclinic amphiboles can accept Ca and Na, whereas the smaller [6]-fold site in the orthorhombic amphiboles can accept only Fe^{2+}, Mg and smaller cations. Papike & Ross (1970)

suggested that size plays a role in the distribution of tetrahedral Al in gedrite.

(ii) *strongly polarizing cations:* strongly polarizing cations like Fe^{2+} to form more covalent bonds with oxygen, and hence will prefer the M(4) site (Ghose 1961, 1965). Strongly polarizing cations will tend to avoid each other. In addition, strongly polarizing cations tend to distort the octahedral sheet and hence will be repelled from the M(1) and M(3) sites, in accord with the fact that in orthopyroxene-cummingtonite assemblages (Kranck 1961), orthopyroxene is more Fe^{2+}-rich than the co-existing cummingtonite (Ghose 1965).

(iii) *relief of strain in the Si–O–Si bond:* Devore (1957) suggested that tetrahedral Al is more likely to order in the T(1) site as the occupation of this position by Al causes fewer Si^{4+} cations to share more than two anions with other Si^{4+} cations, hence relieving the strain in the Si–O–Si bond.

(iv) *steric considerations:* when M(4) is occupied by Ca or Na, Ghose (1965) proposed that the O(4) atoms recoil away from the M(4) site, causing an anticlockwise rotation of the T(2) tetrahedron; substitution of Al into T(1) will cause T(1) to rotate clockwise to compensate for this rotation.

Certain remarks are in order concerning some of the mechanisms proposed above. Firstly, the use of ionic size to forecast site-ordering patterns is of use only in exaggerated cases, where gross differences in cation radius occur. In general, the co-ordination polyhedron of a cation adjusts to accommodate its constituent cation, and its size is irrelevant to the possible occupancy of other cations, with the exception that the normal radius-ratio rules will probably apply. With regard to the possible effect of highly polarizing cations, Fe^{2+} does prefer the M(4) site in the iron–magnesium–manganese amphiboles (Ghose 1961, Finger 1967, 1969a, 1970b) and in tremolite (Goldman & Rossman 1977a). However Mn^{2+} has an even higher preference for the M(4) site in the Fe–Mg–Mn amphiboles (Bancroft et al. 1967a, Hawthorne & Grundy 1977b) that is not in accord with this mechanism. In addition, if strongly polarizing cations tend to avoid each other, then there should be a lack of clustering of Fe^{2+} cations in the structure. Except for the cummingtonite–grunerite series, this is not in accord with the infrared absorption results of Strens (1966), which indicate significant clustering of Fe^{2+} (and Mg) in holmquistite, glaucophane, riebeckite, tremolite and anthophyllite.

Brown & Gibbs (1970) have examined cation

ordering in the tetrahedral part of silicate structures in terms of the predicted bond-orders of the cation–anion pairs involved. In general, T–O(br) bonds involved in wide T–O(br)–T linkages are of higher bond-order than those involved in narrow T–O(br)–T linkages. As Al(+B, Be and Mg) has a lower π-bonding potential in tetrahedral co-ordination than Si, Si should then prefer those tetrahedral sites involved in the widest average T–O–T angles. Brown & Gibbs (1970) noted that the results for potassian titanian magnesio-hastingsite(24), potassian pargasite(38) and potassian titanian pargasite(39) are not compatible with this argument, as the average T–O(br)–T angle is larger for T(1) (the Al-rich site) than for T(2); they suggested that the factor on which this rule is based is overridden by the fact that the O(4) anion is the only oxygen in the structure that may have a lone-pair orbital available for strong π-bond formation, and hence Si is ordered in the T(2) site. They also noted that the ordering of Be and Si in joesmithite(25) can be rationalized in a similar manner. Although couched in terms of a covalent-bond model, the latter argument of Brown & Gibbs (1970) is similar to the charge-balance approach outlined earlier. If the T–O(br)–T criterion is to be used, it is not sufficient to compare the observed angles at the various sites in the structure. Rather it is necessary to compare the observed T–O(br)–T angles in the structure with those angles that would result from the alternate cation distribution(s). Thus this method is now practical, with accurate modeling by D.L.S. methods.

Crystal-field-stabilization energy

Another criterion that has been used to rationalize site preferences of transition metals, particularly Fe^{2+}, is based on crystal-field theory (Ballhausen 1962, Griffith 1961). In the free ion or in a spherically symmetrical potential-field, the $3d$ orbitals are energetically degenerate. Application of a potential field of lower symmetry removes the complete degeneracy of the orbital-energy levels, as the reducible representation spanned by these orbitals must contain the irreducible representations of the symmetry group. High-spin Fe^{2+} has a d^6 configuration, and thus the lowest-energy $3d$ orbital is occupied by two electrons; as the average energy of the five orbitals is equal to the energy of the degenerate levels in a corresponding spherically symmetrical crystal-field, the difference between this value and the energy of the lowest-energy $3d$ orbital thus enhances the stability of the undegenerate configuration and is known as the crystal-field-stabilization energy (C.F.S.E.). Thus the greater the orbital energy-level splitting, the greater the C.F.S.E. term; hence Fe^{2+} will tend to occupy the site with the largest C.F.S.E. term.

Several studies have attempted to correlate C.F.S.E. with nearest-neighbor configuration on the assumption that the bonded anions reflect the strength and symmetry of the crystal field. According to this argument, increased distortion will produce a greater splitting of the energy levels, thus enhancing the C.F.S.E., providing the "bond type" is identical in each co-ordination polyhedron (Burns 1968a, b, 1970a). The agreement with observed patterns of ordering is not particularly good, as Fe^{2+} is commonly enriched at the M(1) and M(3) sites as compared with the predicted enrichment at the M(2) site. Several factors are pertinent to the use of this criterion. Firstly, the effects of polyhedron distortion on the C.F.S.E. are not well understood. Variation in individual bond-lengths *and* variation in bond angles affect the magnitude of the orbital splitting. Some studies have examined the effect of varying bond-angles in a simple systematic way (Krishnamurthy & Schaap 1970, Garner & Mabbs 1970) with constant bond-length; the relative orbital-energy levels are considerably affected by this. The effect of variation in individual bond-lengths (with a constant mean bond-length) is not well characterized. Thus, deciding which of two irregular pseudo-octahedral co-ordinations is the more irregular with regard to estimating the larger C.F.S.E. is extremely difficult unless gross differences occur. Another factor that may influence the magnitude of the C.F.S.E. is the effect of next-nearest-neighbor ions. This factor has been examined by Jäger & Perthel (1967, 1970), who concluded that non-co-ordination ions have considerable effect on orbital splitting in an octahedral environment. Thirdly, the C.F.S.E. is dependent on the *local* environment in the crystal (Manning 1973), not on the average environment as characterized by crystallographic studies, and this may also significantly affect the orbital splitting (Das 1965). Thus, using the average configuration of the co-ordination polyhedra in a structure is not strictly applicable unless that structure is an Fe^{2+} end-member.

Ribbe & Gibbs (1971) have suggested that the C.F.S.E. may also be a function of anion type, noting that Dq (a measure of the orbital splitting in an octahedral crystal-field) decreases

along the spectrochemical series for octahedrally co-ordinated $Fe^{2+}X_6$ groups. Consequently Fe^{2+} will tend to avoid sites co-ordinated by F, as suggested by the site populations exhibited by fluor-richterite(34) and (35). This argument is supported by data for micas (Rosenberg & Foit 1977) and humites (Ribbe & Gibbs 1972).

The C.F.S.E. method, as with the Madelung-energy and site-potential methods, predicts ordering on the basis of part of the total structure-energy, with the assumption that the remainder of the structure-energy terms remain constant and thus do not contribute to the ordering process. A much more general method has been suggested (Strens & Wood 1970, Wood & Strens 1970), but considerable difficulties remain to be solved before successful application.
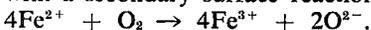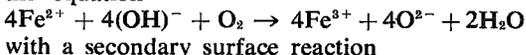
General considerations

There has been considerable confusion between site occupancy, which is an experimental result, and site preference, which is an *interpretation* of an experimental result. Consider the Fe–Mg–Mn amphiboles. In the magnesio-cummingtonite – grunerite series, Fe^{2+} shows the site occupancy $M(4) > M(1) \sim M(2) \sim M(3)$, whereas in the grunerite – dannemorite series, Fe^{2+} shows the site occupancy $M(4) < M(1)$, $M(2)$, $M(3)$; in both cases, the pattern of site occupancy presumably reflects the Fe^{2+} site-preference in the presence of Mg and Mn, respectively. In the ternary Fe–Mg–Mn amphiboles, Fe^{2+} may show the site occupancy $M(4) > M(1)$, $M(2)$, $M(3)$ or $M(4) < M(1)$, $M(2)$, $M(3)$, depending on the amount of Mn in the amphibole; with regard to Mg, Fe^{2+} shows the site preference $M(4) > M(1)$, $M(2)$, $M(3)$; with regard to Mn, Fe^{2+} shows the site preference $M(4) < M(1)$, $M(2)$, $M(3)$, whereas based on the observed site-occupancies, the site preference of Fe^{2+} changes with composition. Similar effects may occur in such combinations of cations as (Mg, Fe^{2+}, Mn), (Mg, Fe^{2+}, Li) or $(Mg Fe^{2+}, Zn)$, and it is probably simpler to refer to cation-ordering patterns rather than site preferences, particularly in amphiboles.

OXIDATION–DEHYDROXYLATION IN AMPHIBOLES

The behavior of amphiboles on heating has been the subject of a large number of studies over the past one hundred years. Early studies were prompted by the similarity of heated horn-blende to "basaltic hornblende", and by the controversy concerning the origin of the pecu-liar optical properties of "basaltic hornblende". Much of the early work is summarized by Barnes (1930), who noted three different views of the changes in hornblende upon heating: (i) oxidation of $Fe^{2+} \rightarrow Fe^{3+}$, (ii) dehydration, and (iii) inversion (phase transformation). Barnes (1930) performed extensive heating experiments on amphiboles both in air and in hydrogen, showing that: (i) iron-poor amphiboles do not change upon heating whereas iron-bearing amphiboles heated in air show a marked conversion of $Fe^{2+} \rightarrow Fe^{3+}$ and a loss of water, generally changing color from green to brown; (ii) the weight loss on heating (to 800°C) is only a fraction of the water obtained by analysis, and (iii) iron-bearing amphiboles do not change when heated in hydrogen. In addition, brown hornblende changes back to green hornblende upon heating in hydrogen. From this, Barnes (1930) concluded that oxidation of Fe^{2+} to Fe^{3+} occurs upon heating iron-bearing hornblende, accompanied by dehydration where hydrogen was given off, allowing the oxidation to proceed.

Addison *et al.* (1962a, b) examined the oxidation of crocidolite by heating in specific atmospheres and measuring the products generated. They heated crocidolite in air, oxygen and vacuum, resulting in partial oxidation of the crocidolite and loss of uncombined water, and proposed that oxidation involves simultaneous oxidation of Fe^{2+} and OH according to the equation

$$4Fe^{2+} + 4(OH)^- + O_2 \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$$

with a secondary surface reaction

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}.$$

The surface reaction is maintained by the migration of electrons and protons through the crystal. Incomplete oxidation at the temperature of study (450°C) was attributed to a blocking interaction by Mg cations at the octahedrally co-ordinated sites, hindering electron migration along the Z direction (Addison & White 1968a). Addison *et al.* (1962b) performed rate studies on the oxidation of crocidolite and found that oxidation at constant partial pressure of oxygen proceeds at a constant rate until complete oxidation occurs (between 350 and 480°C). They also proposed that there is a "strongly held" surface layer of water that inhibits oxidation if the temperature and partial pressure of oxygen are too low. Both studies also indicated that fibre formation in crocidolite produces partial oxidation at ambient temperatures. Rate studies were also carried out by Clark & Freeman (1967). Addison & Sharp (1962, 1968) heated both fresh and oxidized crocidolite in hydrogen, and suggested that zero-valent iron is formed