sodium of type II and oxygen across the eight member ring 2·3 Å. These distances are consistent with the known adsorption properties of the material.

Table 3. *Discrepancy factors*

| Class of reflection | No. of reflections | No. of spectrometer lines | $R$ Reed & Breck | $R$ This investigation |
|---|---|---|---|---|
| Unique observed | 17 | 17 | 0·24 | 0·18 |
| Non-unique observed | 26 | 12 | 0·14 | 0·12 |
| All observed | 43 | 29 | 0·21 | 0·16 |

$R=\Sigma\|F_o\|-\|F_c\|/\|F_o\|$ where $|F_o|$ or $|F_c|$ for a non-unique line $=(\Sigma PF^2/P_{\max.})^{\frac{1}{2}}$.

For the unobserved reflections (25 reflections, 18 lines), three calculate to be slightly above the observational limit, one of these 2·1·1 was observed by Reed & Breck.

For the unique observed reflections the framework atoms alone give an $R=0{\cdot}30$.

Table 4. *Nearest neighbor distances for the refined model*

Distances within the framework tetrahedra

| | $d_{ij}$ | Average distance |
|---|---|---|
| Si,Al–$O_I$ | 1·69 Å | 1·66 Å |
| Si,Al–$O_{II}$ | 1·65 | |
| Si,Al–$O_{III}$ | 1·61 | |
| $O_I$–$O_I'$ | 2·78 | 2·71 Å |
| $O_I$–$O_{II}$ | 2·71 | |
| $O_I$–$O_{III}$ | 2·67 | |
| $O_{II}$–$O_{III}$ | 2·70 | |

Sodium–oxygen distances

| | |
|---|---|
| $Na_I$–$O_{III}$ | 2·27 Å |
| $Na_I$–$O_I$ | 2·14 |
| $Na_{II}$–$O_{II}$ | 2·36 |

Thus far, the refinement has been carried out using the pseudo unit cell for zeolite $A$ rather than the true unit cell with $a_0=24{\cdot}56$ Å. The larger cell of lower symmetry is required because of a very weak reflective indexing $\frac{5}{2}\cdot\frac{3}{2}\cdot\frac{1}{2}$ on the basis of the small cell and is necessary to allow alternation of $SiO_{4/2}$ and $AlO_{4/2}$ tetrahedra according to the ideas of Loewenstein (1942). Also zeolite $A$ is not strictly stoichiometric. Chemical analysis of Lot 4541 gives the atom ratios $Na/Al=0{\cdot}95\pm0{\cdot}04$ and $Si/Al=0{\cdot}98\pm0{\cdot}02$. Si/Al ratios less than 1·0 have been noticed previously for zeolite $A$, Reed & Breck (1956), and the suggestion was made by Barrer & Meier (1958) that an extra $NaAlO_2$ unit is occluded at the center of the $\beta$ cage. The Na/Al ratio less than one may indicate cation defects in the structure or a few per cent of hydrogen exchange. Because of these many factors, further refinement of the structure does not seem justified until single crystal data is available.

It is a pleasure to acknowledge the help of Mr L. G. Dowell who aided in the experimental phases of this investigation; Mr L. D. Potts who wrote the program for the Burroughs 205 computer; and Dr D. W. Breck who aided and supported the refinement of the structure.

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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### Relationships between the crystal chemistry of pyroxenes and amphiboles.

By E. J. W. Whittaker, *Ferodo Ltd., Chapel-en-le-Frith, Stockport, England*

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In a recent paper (Whittaker, 1960) it has been shown that the composition ranges of the orthorhombic amphiboles, and the different $\beta$ angles and $a\sin\beta$ values of the various series of monoclinic amphiboles, depend to a large extent on the radii of the metal ions occupying certain sites in the structure. It is therefore natural to enquire whether the same or a similar dependence can be observed in the related field of the pyroxenes.

The amphibole structure may be regarded as a packing together of narrow strips of talc-like structure. The

pyroxene structure (Warren & Bragg, 1928; Warren & Biscoe, 1931) may also be regarded as being built up from similar strips, although they are so narrow that the resemblance to the talc structure is much less obvious. Because these strips are so narrow there is no metal ion site in the pyroxene structure which is not involved at all in linking the strips together. The two sites $M_1$ and $M_2$ in the pyroxenes correspond to the sites $M_2$ and $M_4$ respectively in the amphiboles in respect of their degree of involvement in the packing of the strips. The $M_2$ of pyroxene also corresponds to the $M_4$ of amphibole in that it is the site which can be occupied by the larger ions such as calcium or sodium. If the pyroxenes were to conform strictly to the principles which have been shown to be applicable to the amphiboles, it would follow that:

(*a*) The purely magnesian pyroxene would be orthorhombic (corresponding to anthophyllite), but the replacement of any appreciable proportion of the magnesium by ferrous iron would lead to an immediate transition to a monoclinic structure (corresponding to cummingtonite).

(*b*) Pyroxene phases containing ions other than magnesium would be orthorhombic only if (i) neither ion were larger than Mg (e.g. $M_1$=Al, $M_2$=Li), *or* (ii) ferrous iron were present at $M_2$ and a compensating substitution of a smaller ion (Al or Fe‴) for magnesium occurred at $M_1$ (corresponding to gedrite).

These conclusions do not correspond with the facts. The purely magnesian pyroxene, enstatite, is orthorhombic, but it will tolerate substantial replacement of Mg by Fe″ while maintaining the orthorhombic structure (i.e. in hypersthene). On the other hand the purely magnesian pyroxene is dimorphic and is also known in the monoclinic form, clinoenstatite, while the lithium aluminium pyroxene, spodumene, is monoclinic although no ion is involved larger than Mg. Unfortunately there seems to be no known pyroxene containing balanced replacement of Mg by Fe″ and Al, or by Fe″ and Fe‴ (with of course further replacement of Si by Al to preserve the charge balance), so that it is not known whether such a pyroxene analogue of a gedrite would be orthorhombic.

Thus the orthorhombic pyroxene structure is formed under roughly similar conditions of ion size to those which lead to the orthorhombic amphibole structure, but the limiting conditions are far less rigidly defined. A possible explanation for this is that the single $SiO_3$ chain might be expected to be more flexible than the double $Si_4O_{11}$ chain. Then, if the introduction of different-sized ions leads to distortion of the chain, it will at the same time modify the conditions for stability of the orthorhombic and monoclinic structures. There is some evidence that this is in fact the case since there are appreciable differences in the relative positions of the silicon and oxygen atoms in the three pyroxene structures that have been published—diopside (Warren & Bragg, 1928), enstatite (Warren & Modell, 1930) and spodumene (Warren & Biscoe, 1931).

The parallelism between the relationships of $\beta$ and ionic size at $M_2$ in pyroxenes and $M_4$ in amphiboles is quite close as shown in the following table:

| Ion | $\beta$ in amphiboles | $\beta$ in pyroxenes | |
|---|---|---|---|
| Ca | 105° 50′ | 104° 20′–105° 50′ | (Kuno & Hess, 1953) |
| Na | 107° 20′ | 106° 49′–107° 16′ | (Dana, 1932) |
| Mg | 111° | 108° 22′ | (Kuno & Hess, 1953) |
| Li | 111° | 110° 20′ | (Warren & Biscoe, 1931) |

The values given for the amphiboles are those, interpolated or extrapolated as necessary to the nearest 10′, from the graph relating $\beta$ to the radius of $M_4$ (Whittaker, 1960). They relate to the *I*-centred amphibole cell. The values given for the pyroxenes have been converted to the obtuse values from the acute values given in the literature and relate to the *C*-centred pyroxene cell, which is structurally analogous to the *I*-centred amphibole cell. The parallelism is quite marked, though again it is clear that there is a disturbing influence of the size of the ion at $M_1$ in the pyroxenes; as this increases, there is a systematic decrease in $\beta$ with a given ion size at $M_2$ as follows:

| $M_2$ | | $M_1$ (predominant ion) | | | |
|---|---|---|---|---|---|
| Chemical symbol | Radius (Å) | Chemical symbol | Radius (Å) | $\beta$ | $a \sin \beta$ |
| Ca | 1·06 | Fe″ | 0·83 | 104° 20′ | 9·55 |
| | | Mg | 0·78 | 105° 50′ | 9·38 |
| Na | 0·98 | Fe‴ | 0·67 | 106° 49′ | |
| | | Al | 0·57 | 107° 16′ | |
| Mg | 0·78 | Mg | 0·78 | 108° 22′ | 9·12 |
| Li | 0·78 | Al | 0·57 | 110° 20′ | 8·91 |

Irregularities in the $\beta$ values of the amphiboles are not so obviously attributable to a particular factor.

The above remarks on the effect of ionic size on $\beta$ also apply to the effect on $a \sin \beta$, where this is known. This spacing is substantially more variable than in the amphiboles (pyroxene range 0·64 Å; amphibole range 0·27 Å). It is also notable that the structural readjustments in spodumene permit it to achieve a value of $a \sin \beta$ which is lower than the value of $a/2$ in enstatite (9·10 Å).

Data from pigeonites have been excluded from the above discussion in view of the evidence that they have a different space group from the other pyroxenes (Bown & Gay, 1957).

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