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RECALCULATION OF PYROXENE ANALYSES

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In the crystal structure of any pyroxene there are three sets of cation sites which we may designate A (coordination 6 or more), A' (coordina- tion 6), and B (4-coordinated), in the ratio represented by $A'AB_2O_6$, for example $CaMgSi_2O_6$ (Warren and Bragg, 1929; Warren and Modell, 1930; Morimoto, *et al.*, 1960). For the present purpose A' and A are not differentiated, so that the formula may be written $A_2B_2O_6$. In rock- forming pyroxenes the B sites contain mainly Si, with usually some Al, and apparently occasionally a few Fe^{3+} and Ti ions if the B sites are not filled by the available Si and Al ions. To save repetition the ability of Fe^{3+} and Ti to act as Al in some circumstances will not be mentioned again. All cations other than Si may occupy the A sites. Al can thus be present in both A and B positions.

After recalculating to six oxygens the ionic proportions obtained from the chemical analysis of a pyroxene, the cations may be assigned to A and B positions. All the Si must go in B, all other cations except Al in A. There are three ways which have been used to partition the Al ions between A and B:

1. to split the Al ions so that $\Sigma A = \Sigma B$.
2. to make $\Sigma B = 2$ by adding Al, the rest of the Al (if any) falling into A.
3. by the method proposed by Hess (1949), in which the ions are allocated in stages corresponding to the building of formula units such as $NaCrSi_2O_6$, etc. The (WXY) group of Hess corresponds to A above, the Z group to B.

In practice with a good analysis there is little difference between the

results of the three methods. The third method is the most complicated but was claimed by Hess to be superior, in that it was devised to obey two principles, which by implication were not obeyed by other methods. These principles are:

1. That the sum of the ionic charges in A and B must balance those of the anions at each stage in the assignment of ions.
2. That the numbers of ions A, B and O at each stage must be in ratio 1:1:3, or 2:2:6, as demanded by the pyroxene structure and formula.

It is clearly true that *overall charge balance* must be achieved, but this will occur automatically in any method of recalculation (aside from arithmetical error), since the analysis is cast in the form of oxides. There is no significance in the requirement that a balance should be achieved at each stage, unless it is envisaged that the different stages represent different unit cells, in which case the requirement is that of *local charge balance*, or of unit cell neutrality. It is not clear that this is what Hess had in mind, but it is a situation unlikely to be realized in practice, particularly in quickly cooled igneous pyroxenes.

Regarding the second principle, an overall *number balance* is certainly valid for a perfect analysis of a pyroxene without unoccupied sites. In an actual analysis, however, it is common experience that the total cation: oxygen ratio is usually *not* exactly 4:6, so that the ratio 2:2:6 cannot be attained throughout. In Hess' description of his method this is not apparent, since the ratio is maintained at each of his numbered stages 1 to 6. In the un-numbered last stage, that of putting the remaining divalent cations into A and the remaining Si into B, the number balance must fail unless the total cation:oxygen ratio equals 4:6 exactly. If the principle cannot be maintained at every stage, it seems illogical to insist on it in the first stages. There is also the possibility that defect pyroxenes may exist, in which some of the cation sites are not occupied. Evidence to support this hypothesis has been put forward by Boyd and England (Abelson, 1960).

Nevertheless the third method "seems to work," that is, the totals in A and B are close to 2 for a good chemical analysis. To compare the 3 methods the following study was made.

Suppose that a perfect chemical analysis would give ionic proportions $p(1+$ cations$)$, $q(2+)$, $r(3+)$, $s(4+$ not Si$)$, t(Si) and u(oxygen). Then, by overall charge balance we have

$$p + 2q + 3r + 4(s + t) = 2u$$

In a perfect pyroxene structure without defects the total of cations equals two-thirds the total of oxygens. We can allow for the possibility of defect pyroxenes by writing

$$3(p + q + r + s + t + \delta) = 2u$$

δ being the number of vacant cation sites per u oxygens. The ionic proportions given by an actual analysis are written $p' = p + dp(1+)$, etc. Charge balance will still apply, so that

$$p' + 2q' + 3r' + 4(s' + t') = 2u'$$

and, by difference,

$$dp + 2dq + 3dr + 4(ds + dt) = 2du$$

In any recalculation the ionic proportions are multiplied by $6/u'$ to give 6 oxygens. The total number of cations is then

$$\Sigma A + \Sigma B = \frac{6}{u'} (p' + q' + r' + s' + t')$$

which is easily converted, using the equations above, to the form

$$\Sigma A + \Sigma B = 4 - \frac{2}{u'} (3\delta - 2dp - dq + ds + dt)$$

$$= 4 - \Delta$$

Δ depends on the defect nature of the pyroxene, if any, and on a combination of certain analytical errors. It would be zero for a perfect analysis of a non-defect pyroxene.

In whichever of the three ways mentioned the cations are distributed, their total is $4 - \Delta$ per 6 oxygens.

Clearly method 1. will give $\Sigma A = \Sigma B = 2 - \frac{1}{2}\Delta$, while method 2. makes $\Sigma B = 2$, so that $\Sigma A = 2 - \Delta$. The totals obtained in method 3. can be found from the following grouping of the various stages. For convenience, the normalization to 6 oxygens is left until the end.

(a) All the p' $(1+)$ cations are paired with $p'(3+)$ cations in the A sites, with Si in B and oxygen to balance. (Na−Cr, Na−Fe, Na−Al).

(b) All the $s'(4+\text{non-Si})$ cations are paired with $s'(2+)$ cations in the A sites and balanced by $2s'(3+)$ cations in B, and of course oxygen. (Ti−2Al).

(c) The remaining $(3+)$ cations, $(r' - p' - 2s')$ in number, are split equally between A and B sites. (Fe−Al, Cr−Al, Al−Al).

(d) The remaining $(2+)$ cations are put in A, and the remaining Si ions in B.

(e) The A and B totals are normalized to 6 oxygens, the factor being $6/u'$ as before.

The total occupancy of B sites is all the t' Si plus $2s'(3+)$ ions from (b) and $\frac{1}{2}(r' - p' - 2s')$ from (c), thus

$$\Sigma B = \frac{6}{u'} \left[t' + 2s' + \frac{1}{2}(r' - p' - 2s') \right]$$

This is easily converted, using the three basic equations, to the form

$$\Sigma B = 2 + \Delta$$

where Δ is the same expression as before. Since the total number of cations has been shown to be $4 - \Delta$, clearly $\Sigma A = 2 - 2\Delta$, and this can be confirmed by straight additions as for ΣB.

Looking through the analyses worked out in the Hess (1949) paper, one finds that ΣA does generally differ from 2 by twice the amount that ΣB does, and in the opposite direction, as predicted. In some analyses this does not appear to be so, but detailed investigation has always revealed an arithmetical error of one sort or another in the recalculation of the analysis. This underlines the point that the Hess method is quite complicated and errors are prone to creep in; at the very least the present work provides a check on the arithmetic.

It is now clear why method 3. "works," despite the fact that the principles of its operation are open to challenge. One may nevertheless ask whether the method gives a more correct distribution of Al ions, whether in fact it allows better for the errors in analysis than do methods 1. and 2. It is not clear that this is the case, firstly since the method was not specifically constructed to do this, and secondly since all the error is concentrated into one stage, the last. As far as the first two methods are concerned equal weight is given to the errors in all constituents. It has already been noted that for a good analysis it does not much matter which method is used. The % Al content of the B sites is particularly sensitive; for example take Analysis No. 22 of Hess (1949) — the % Al in B has values of 4.0% for 1., 4.4% for 2. and 5.3% for 3.

The results of all three methods of recalculation depend on the same quantity Δ, which is easily found since the total number of cations per six oxygens is $4 - \Delta$. Δ may be positive, zero or negative. Whichever form of recalculation is favored one can partition the Al so as to give the values of ΣA and ΣB as calculated here in terms of Δ. In particular the full Hess procedure can be short-circuited even if the Hess method is chosen.

If Δ is positive it is preferable, since defects are more likely to occur in A than in B sites, to use method 2. thereby making $\Sigma B = 2$ and concentrating the deficiency in A. If Δ is negative however the error is best spread by making $\Sigma A = \Sigma B$ according to method 1. There seems to be little to commend method 3.

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ABSENCE OF OPTICALLY POSITIVE POTASH FELDSPAR IN THE INYO MOUNTAINS, CALIFORNIA-NEVADA

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An unusual, untwinned potash feldspar of low refractive index and positive sign was reported by Anderson (1937, p. 11) to be abundant in the Boundary Peak granite of the Northern Inyo Range, California-Nevada. The mineral, tentatively identified as the "isorthoclase" of Duparc (1904), was studied in more detail by Anderson and Maclellan (1937). By x-ray, universal stage and spectroscopic techniques this mineral was found to be an optically positive, triclinic potash feldspar ($Or_{72}Ab_{26}An_2$) with $2V\gamma = 64$–$89°$, $\alpha = 1.518$, $\beta = 1.520$, $\gamma = 1.524$. This description more closely fits the "isomicrocline" of Kazakov (1959).

Optically positive potash feldspars (isomicrocline, isorthoclase, isosanidine) have been reported from several other areas (Barth, 1933; Duparc, 1904; Kazakov, 1956; Luczizky, 1905; Tsuboi, 1936). As indicated by Smith and MacKenzie (1961) further study by x-ray as well as optical techniques is needed before these feldspars can be fitted into the overall feldspar classification.

Attempts to obtain a sample of the original material from the collections of Anderson or Maclellan (both of whom died early in life) and from the x-ray laboratory of Dr. Linus Pauling were not successful. During the course of the author's studies of granitic rocks in the Inyo batholith (Emerson, 1959), the feldspars from over one hundred samples of Anderson's Boundary Peak granite were examined. No optically positive potash feldspar was found when conoscopic figures were checked on the flat stage or, in doubtful cases, on the universal stage. In addition, the potash feldspars of ten samples from the Boundary Peak granite "type" areas on the east face of Montgomery Peak and in Middle Canyon were studied in thin section. Direct measurements between optic axes were made with a universal stage using the Leitz UMK 50X/0.60 N.A. objective and conoscopic light. All of the potash feldspar was found to be optically negative, intermediate to maximum microcline (Tuttle, 1952) with $2V\alpha = 62$–$86°$. Figure 1 shows the $2V\alpha$ distribution of fifty grains from the "type"