CONTRIBUTION TO THE STUDY OF SEPIOLITE: II. SOME CONSIDERATIONS REGARDING THE MINERALOGICAL FORMULA[1]

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ABSTRACT

It is suggested that the minerals of the palygorskite-sepiolite group occupy the region of discontinuity between dioctahedral and trioctahedral minerals. There is thus a series of minerals, the two extremes having a planar lattice, and the intermediate members a fibrous lattice. The lamellar-fibrous change in structure takes place as the number of vacancies increases progressively.

Among the minerals of fibrous structure, the structural change from sepiolite to attapulgite occurs in such a way as to allow no more than one vacancy per structural fiber, and per half cell, as if this vacancy were not distributed at random, but symmetrically among the octahedral positions. The greater the number of vacant octahedral positions, the smaller the extension of the octahedral layer. The margin of variation in the number of vacant octahedral positions per structural fiber is greater in sepiolite than in attapulgite, probably because of the greater width of the fiber in the former mineral.

INTRODUCTION

Outstanding contributions to the study of the fibrous minerals of the palygorskite-sepiolite group have been made by Fersmann, Lapparent, Migeon, Longchambon and Caillère. The fundamental contribution, however, is that of Bradley, who proposed a structural scheme for both minerals (Bradley, 1940; Nagy and Bradley, 1955).

We have revised some ideas previously published by us (Martín-Vivaldi and Cano-Ruiz, 1953) in the light of Nagy and Bradley's (1955) structure for sepiolite, using our own published analyses, numerous data from the literature, and new analyses on six fractions of different particle size separated from Spanish sepiolites.

The purity of the new samples was checked by chemical analysis, determination of free silica, cation-exchange capacity, thermal weight-loss curves, D.T.A., and x-ray powder diagrams. Results from two of the samples were rejected for this study, on account of their high quartz and silica gel content.

Approximately fifty sepiolite analyses were used, together with about twenty analyses of attapulgites, montmorillonites, nontronites and saponites.

As a result of this revision, certain points have been confirmed, and we have found new relations between minerals of lamellar structure and those of fibrous structure, which seemed to us worthy of presentation here.

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[1] For the first paper in this series, see Martín Vivaldi and Cano Ruiz (1953).
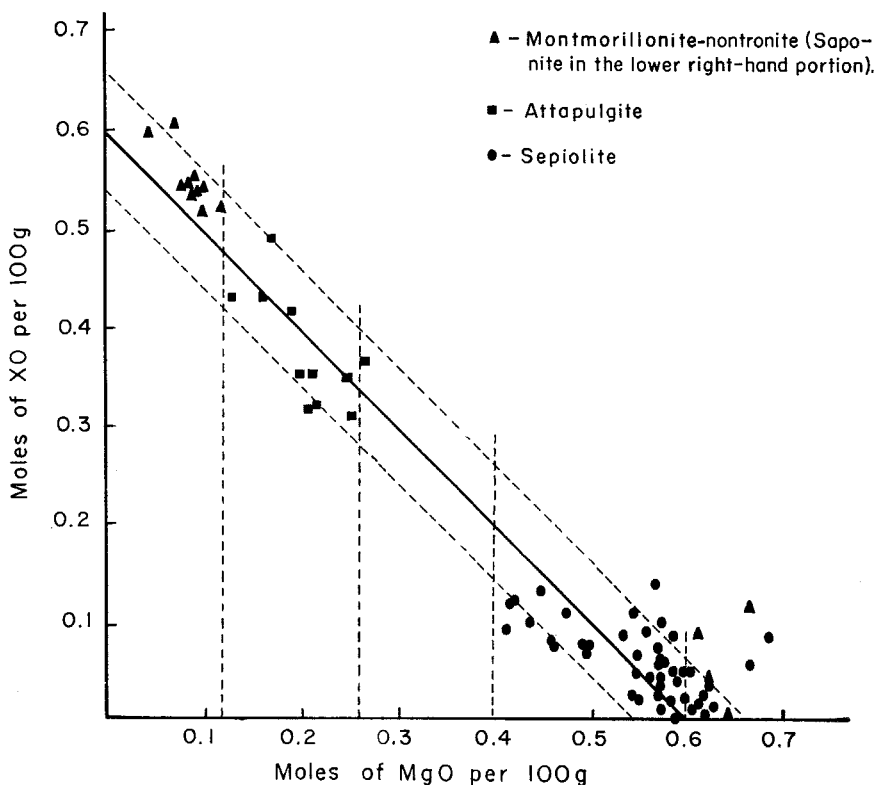
173

FIGURE 1.— Moles of MgO vs. moles of XO for montmorillonites, nontronites, saponites, attapulgites, and sepiolites.

DISCUSSION

From all the sepiolite analyses, a mean value of 53.9 percent silica is obtained, with a standard error of $\pm$ 1.9. The mean number of octahedral cations calculated as RO[1] is 0.6 moles per 100 g, equivalent to about 24 percent MgO. From Nagy and Bradley's (1955) structural formula, $6SiO_2 \cdot 4MgO \cdot 4H_2O$, adding four extra molecules of water to make it comparable with the analytical data, we obtain for the silica 54.2 percent, and for the MgO 24.2 percent.

Calcium was not included in this calculation, since it was not considered as belonging to the lattice, for the reasons given in a previous publication (Martín Vivaldi and Cano Ruiz, 1953), though this point may need reconsideration.

The histograms, especially of RO, are normal, and the mean is the most probable value.

[1] $RO =$ moles MgO + moles (Fe_2O_3 + Al_2O_3 + FeO + MnO), the latter expressed as MgO.

Figure 1 shows XO (moles of Al_2O_3 + Fe_2O_3 + FeO + MnO expressed as MgO) as a function of the MgO molar content. If the hypothesis of an equivalent isomorphous replacement of Mg by Fe^{3+}, Fe^{2+}, Al^{3+}, Mn^{2+} is correct, the points ought to fall on a straight line inclined at 135°, cutting the abscissa and ordinate at 0.6. The cloud of points is distributed approximately around this line, and almost all of them are within a distance of $\sigma = \pm$ 0.06, the standard error of the mean of RO. This representation confirms that even the wholly magnesian end member does not have more than 0.6 molecules of MgO, not enough therefore to occupy the 18 octahedral positions in the cell; two are left unoccupied, although the inversion of tetrahedra does not give rise to any loss of octahedral positions, compared with the planar lattice. Furthermore, the margin of isomorphous substitution of Mg by trivalent cations is small, and only in a few samples does this substitution go so far as to create two extra holes. The number of holes permitted is thus fewer than two in every nine positions.

Making the same calculation with saponite, attapulgite, montmorillonite and nontronite, we find the following facts: (1) In ideal, wholly magnesian attapulgite, only 15 out of 18 positions are occupied, in accordance with Bradley's structure. (2) Actual attapulgite minerals have a degree of substitution such that one out of every five positions is unoccupied. (3) In sepiolite, in which the (elementary) fiber contains nine octahedral positions, about two holes are permitted; whereas in attapulgite, in which the fiber contains five positions, only one hole is permitted. (4) Montmorillonite, nontronite and saponite are arranged on another straight line parallel to the one already mentioned, corresponding to 18 octahedral positions. Almost all these positions are occupied in saponite, leaving at the most one empty out of nine, and in the dioctahedral minerals three out of nine. (5) The zone corresponding to montmorillonite does not overlap that of attapulgite, if Miss Foster's (1951) revised data are used instead of Ross and Hendricks' (1945); i.e., taking account of exchangeable Mg.

To summarize, the foregoing study seems to indicate that, at least in the minerals studied, a planar lattice exists when the number of vacant positions is small. When a proportion of one vacant position in nine is reached, the structure is that of sepiolite, the layer being interrupted at each ninth position. With progressive substitution tending to two or more vacancies in each nine positions, there are no known minerals until we reach those with attapulgite structure, in which the layer is interrupted at each fifth position, one position being vacant and four occupied. With still more substitution, and a correspondingly larger number of vacancies, fibrous minerals should appear in which the layer is interrupted every third position, if the vacant position, as in the other minerals, is to be placeable symmetrically in the fiber. Such minerals would be very unstable; in fact, other minerals with planar lattice appear (montmorillonite, nontronite), in which the octahedral holes can be distributed symmetrically.

The breaks in the diagram would correspond to sepiolite-group minerals having more than two vacant positions in every nine, or attapulgite-group minerals with more than one in every five. If we still suppose that the vacant positions must be symmetrically situated, the region of the breaks might correspond to minerals with their octahedral layers interrupted once in every

seven positions, six positions being occupied. However, no system of inversion of tetrahedra can be imagined which gives a structure of this sort.

The above considerations are not intended to suggest that there is a genetical relationship in nature between the different minerals of these groups, but only that the cause of the discontinuity between diocta- and trioctahedral minerals may lie in the fact that the energy conditions favor a planar lattice when there are practically no vacancies in the octahedral positions, or when there is one vacancy in three positions. In intermediate cases, there is a preference for the fibrous lattice, in which the octahedral layer is interrupted in such a way that the vacancies may be distributed symmetrically.

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