CONTRIBUTION TO THE STUDY OF SEPIOLITE:
III. THE DEHYDRATION PROCESS AND THE TYPES
OF WATER MOLECULES

By
J. L. MARTIN-VIVALDI AND J. CANO-RUIZ
Estación Experimental del Zaidín, Instituto de Edafología y Fisiología Vegetal,
Granada, Spain

ABSTRACT

A detailed study has been made of the dehydration of sepiolite. This work, together with
other studies of dehydration in vacuo and over phosphoric anhydride, rehydration of samples
heated to various temperatures, specific surface, water uptake, and x-ray examination of
natural and heated samples (to be published later), lead us to certain conclusions regarding
types of water in sepiolite. A comparison is made with attapulgite.

INTRODUCTION

In a previous publication (Martin Vivaldi and Cano Ruiz, 1953) we reported
a study of various Spanish sepiolites, and we attempted to define the SiO₂/MgO
ratio for an ideal, wholly magnesian sepiolite. In addition, we defined the
SiO₂/H₂O ratio and the several types of water present by utilizing the loss on
calcination and dehydration curves for samples which had been in equilibrium
with the vapor pressure above 50 percent sulfuric acid at 20 °C.

From these studies we came to the conclusion that the chemical formula ought
to be 6SiO₂ · 4MgO · 7H₂O, and our conclusions on the distribution of the seven
water molecules were as follows: four are lost in the first branch of the curve
(to 250 °C), two in the second (to 650 °C), and one in the third (to 900 °C).
We also concluded that the loss of the four water molecules at low temperatures
was reversible, so that the structural water was reduced to three molecules.

A previous statistical study (Martin Vivaldi and Cano Ruiz, 1955), utilizing
numerous analyses from the literature, in the light of the structure recently
proposed by Nagy and Bradley (1955), has confirmed fully the ratio 3SiO₂/
2MgO deduced from this structure, so that the chemical formula per half cell
for the totally dehydrated mineral is 12SiO₂ · 8MgO for an ideal, completely
magnesian sepiolite. In this formula the oxides of the cations (Fe³⁺, Fe²⁺, Al³⁺,
and Mn²⁺), which substitute for Mg isomorphically, are expressed as MgO.
This study also showed that a maximum of only eight out of the nine octahedral
positions which occur in each half cell are occupied, so that it is necessary to
introduce two protons to re-establish charge equilibrium, causing an increase
in the structural water content of the mineral.

DISCUSSION AND CONCLUSIONS

A detailed study of the thermal weight-loss curve of sepiolite from Vallecas
(Fig. 1), and of another series of thermal weight-loss curves of the same sample,
obtained during an examination of water uptake, leads to the conclusion that,
with progressive dehydration at increasing temperatures, the water in the Vallecas sepiolite is lost as if it occurred in four positions with different energy. We will designate these as a, b, c and d. In a previous work (Martin Vivaldi and Cano Ruiz, 1953) we suggested that there were three positions, although the possibility of a fourth was indicated even then by the D.T.A. curves and the differential representation of the thermal weight-loss curves.

Of these four classes of water type a is the only one which is altered by the R.H. This type is therefore probably held physically (adsorbed on the surface, and in the structural channels). Calculating the chemical formula of the mineral dried at 250°C, that is to say without the water of type a, we obtain 12SiO₂·8MgO·7H₂O, which is not in accordance with Nagy and Bradley’s structural formula 12SiO₂·8MgO·8H₂O, as regards the number of water molecules belonging to the structure. Of the eight in this formula, Nagy and Bradley consider that four of them are coordinated to the magnesiums along the edges where the octahedral layers are interrupted. The other four are present as OH groups, six of which are normally in this form, and two more formed from the two protons which are necessary to compensate the deficiency caused by the omission of one magnesium per half cell.

If Nagy and Bradley’s structural model is accepted, it is difficult to do without any of the eight molecules of water. We must suppose therefore that a part of the coordinated water (amounting to one molecule) is lost in the same region of temperature as the adsorbed water and the water in the channels. This hypothesis, which may at first seem artificial, is supported by the following experimental facts:

(a) There is a similar anomaly in the dehydration of attapulgite which has a very similar structure (four molecules instead of five), unless we assume a part of the water which is lost in the temperature region corresponding to adsorbed and channel water to be water of coordination. In this case this decision is not so artificial, since the dehydration curve of attapulgite shows a slight inflection at 150°C, which represents a percentage of water (a₁), equivalent approximately to one molecule.

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![Figure 1](image.jpg)

**Figure 1.**—Thermal weight-loss curves of (a) sepiolite from Vallecas and (b) attapulgite from Attapulgus.
(b) This inflection, according to the literature, does not appear with all attapulgites, and when it appears, as in the minerals studied by us (attapulgite from Attapulgus, Ga.), it is not very pronounced.

(c) In Miss Caillère's (1951) studies on sepiolite using the Chevenard balance she finds four regions of water loss, apart from the one corresponding to hygroscopic moisture, one of the regions being near 255° C.

(d) In some D.T.A. curves of attapulgite there is a small endothermic peak immediately following and scarcely separated from the hygroscopic moisture peak.

(e) In our rehydration studies we found that a portion of the a water in sepiolite is lost irreversibly at about 200° C. This water amounts to about one molecule.

(f) Vacuum dehydration of Vallecas sepiolite, at room temperature in the presence of P₂O₅, removes only about 9 percent of water. We must heat to 200° C under these conditions to eliminate an amount of water equal to that lost on the first branch of the dehydration curve. We have observed the same phenomenon with attapulgite under the same conditions.

(g) The specific surface of attapulgite measured by ethylene glycol desorption, according to the Dyal and Hendricks (1950) technique, begins to decrease at about 200° C, proving that at that temperature the structure is being modified.

If therefore we admit the existence of eight molecules of structural water, and if we distribute them in accordance with the percentages derived from each zone of the curve in Figure 1, we obtain the following scheme for the water of constitution:

- a, lost together with adsorbed water 1 mol. per half cell.
- b lost between 250° and 350° C 2.5 mol. per half cell.
- c lost between 350° and 650° C 2.0 mol. per half cell.
- d lost above 700° C 2.5 mol. per half cell.

Since the structural modification takes place at 350° C (according to our x-ray diagrams, and results cited by other authors), this occurs when practically all the coordinated water is lost. In reality we have observed that the transformation begins at about 330° C, that is to say when only about three molecules of coordinated water have been lost. In the modified structure the remaining half molecule of coordinated water probably is highly polarized, giving in fact OH groups, for which reason it is lost in the region belonging to the OH groups formed by the two protons which compensate the gaps in the Mg layer. Lattice water, that is to say the six OH groups which normally belong to this category, is lost above 700° C, although, as often happens during dehydration, half a molecule is lost slowly, probably beginning at 450° C. The reason no doubt is that its energy is comparable with that of the two OH groups arising from the additional protons, and included with the half molecule of coordinated water.

Summing up, we may say that the coordinated water is lost from 150° to 400° C, having three different energies, as a result of progressive dehydration. The molecule of water which is formed at the expense of the two charge-compensating OH's goes off between 360° and 450° C, and the true lattice water is lost above 450° C, slowly at first, then suddenly at 650° C, and slowly again above 700° C.
Our dehydration curve of attapulgite is similar to that of sepiolite, as can be seen from Figure 1. The following differences however can be noted.

First, the molecule of coordinated water $a_4$ has a slightly different energy from the adsorbed and channel water. When it is lost, the remainder of the coordinated water, as in sepiolite, remains with a different energy, going off continuously up to 650°C, and the curve shows no inflection at the temperature at which the structural modification occurs, because this does not alter the energy of the coordinated water loss above 350°C. Finally, the number of molecules of lattice water lost before the structural modification occurs is less than in sepiolite, and the diminution of specific surface between 300°C and 500°C, although it follows a parallel course in the two minerals, is only 25 percent in attapulgite and 40 percent in sepiolite. These facts suggest that the structural modification occurs with more difficulty in sepiolite than in attapulgite, but that when it occurs it is more far-reaching (the x-ray diagram of sepiolite changes, whereas in attapulgite the lines are broadened without changes of position). This is probably connected with the firmer linkage between the structural fibers in sepiolite, the inversion of tetrahedra being along an edge instead of at a vertex.

The results are displayed in Table 1 and Figure 1. We are at present studying samples of different minerals belonging to this group, in order to find out how far the above results are capable of generalization.

REFERENCES


Dyal, R. S., and Hendricks, S. B., 1950, Total surface of clays in polar liquids as a characteristic index: Soil Sci., v. 69, p. 421-432.


—. 1956, Preceding paper, these Proceedings.