NOTE ON WATER OF CRYSTALLIZATION.

By W. W. Coblentz.

IN previous papers[1] on this subject the writer has shown that in substances containing "*water of crystallization*," or "*water of solid solution*" the absorption bands coincide with those of water in its free, liquid state. On the other hand, substances which contain "*water of constitution*" (*i. e.*, the constituents which form water when the substance is heated to a high temperature) do not show absorption bands of water, except hydroxyl groups, which show a band at 3 μ.

The spectroradiometric analysis does not appear to distinguish between water of crystallization and water of solid solution. The absorption bands are identical in position and perhaps in intensity. There are, however, other physical and chemical tests which show a marked distinction between these two forms.

In the process of crystallizing water may enter the substance in varying proportions; but there is a fixed proportion corresponding to a definite compound that is homogeneous and has definite physical properties.[2] On dehydration, the substance becomes inhomogeneous — copper sulphate being a good example. The water escapes at one or more fixed temperature points (and continues to go off at such fixed temperatures until all water is given off) with a sudden change in its properties. On the other hand, in a substance containing water of solid solution or dissolved water, the water is given off gradually throughout a range of temperatures, the physical properties varying with the change in composition. Since there is no loss in homogeneity, and since the water is lost gradually throughout a range of temperatures it cannot be chemically combined. The phenomenon is supposed to be molecular, while in

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[1] Coblentz, Phys. Rev., Vol. 20, p. 252, 1905; Vol. 23, p. 125, 1906. Jahrbuch der Radioaktivitat und Elektronik, III Band, Heft 4. Carnegie Publication, No. 65.

[2] See a clear and concise summary of a recent paper on this subject by Zambonini, given by Professor Hillebrand in Chemical Abstracts, 3, p. 412, 1909.

the crystallization process the behavior would be atomic in its action in order to form a true compound. This leaves an outstanding difference in the interpretation of the various observations which remains unexplained; for the spectroradiometric observations indicate that, both in compounds with water of crystallization and in those of solid solution, the water is present (*i. e.*, has the same physical properties to heat waves) in the same condition as water in its free, liquid state. Selenite, for example, shows the composite spectra of anhydrite ($CaSO_4$) and of water (H_2O); similarly for opal (quartz + water) which is a solid solution. It has been found that the absorption spectrum of a compound is not the composite of the spectra of the constituent elements (*e. g.*, the spectrum of HCl is not the composite of the absorption spectra of H and of Cl, etc.). How then are we to interpret observations on crystallization products? These differences need not disconcert us, for the spectroradiometric test is continually finding new phenomena needing explanation, the most important, perhaps, being the question of density. Ångström[1] has shown that water vapor is more transparent than the liquid phase, when in such layers that the thickness is inversely proportional to the density of the existing phase. A familiar example is (atmospheric) water vapor which transmits the sun's radiation[2] to 11 μ while a layer of water about two centimeters thick, which is equivalent to the water vapor in the atmosphere, absorbs everything beyond 1.2 μ. Recently he has shown[3] that the absorption of the same quantity of CO_2 varies with the pressure, and that if, when under reduced pressure, an inert gas (*e. g.*, hydrogen) is introduced in such quantities that the original pressure is restored, then the absorption bands of the CO_2 increase to their original intensity. These facts are of interest in connection with the experimental data on tremolite given on a subsequent page. In previous work the writer failed to detect water in amphiboles which generally contain a few per cent. of dissolved water. Through the kindness of Dr. E. T. Allen, of the Geophysical Laboratory, an opportunity was granted to examine several samples of tremolites in which he found

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[1] Ångström, Ann. der Phys. (3), 39, p. 267, 1890; (4), 6, p. 163, 1901.

[2] See Carnegie Publication, No. 97, p. 143.

[3] Ångström, Arkiv for Matematik Astronomi och Fysik, 4, No. 3, 1908. Eva von Bahr, Ann. der Phys. (4), 29, p. 780, 1909.

about 2 per cent. of water[1] which is present in solid solution. The sections of the mineral were chosen of sufficient thickness to insure detecting the water, provided its absorption is as great as in the free liquid phase, but as will be noticed presently no water bands could be detected. Its behavior is therefore somewhat like the highly attenuated water vapor in our atmosphere. The bolographs made by Langley[2] show these water bands to be complex and probably shifted slightly towards the short wave-lengths. They show wide absorption bands of water at .92 μ and 1.1 μ which in the liquid are not measurable until the layer has attained a length of about a meter, as shown by Abney and by Julius.

In the present spectroradiometric examination of minerals, a bolometer and fluorite prism were used. The dispersion is much larger than in previous work, so that the absorption bands are much wider than previously found. (See selenite, Fig. 2, and the same specimen described in Carnegie Publication 65, Fig. 2.)

Water (H_2O).

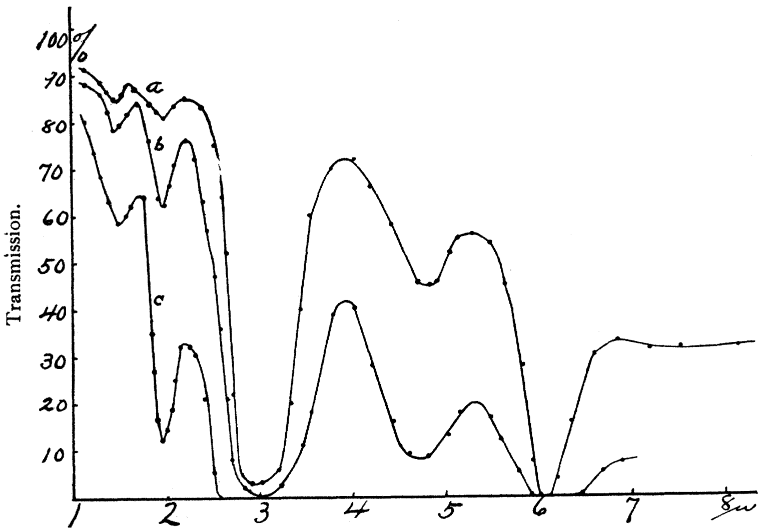

Fig. 2. Water. Curve a; $t = .014$ mm. Curve b; $t = .038$ mm. Curve c; $t = .31$ mm.

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[1] Allen and Clement, Amer. Jour. of Sci., Vol. 26, p. 101, 1908.

[2] Annals Astrophys. Obs., Vol. 1.

In Fig. 1 are given the transmission spectra of pure distilled water, held between two clear plates of fluorite. The thicknesses of the layers of water (accurately determined by placing different thicknesses of tinfoil between the plates) was as follows, viz: Curve $a = .014$ mm., curve $b = .038$ mm. and curve $c = .31$ mm. of water. For thinner layers see Carnegie Publication No. 65 and the PHYSICAL REVIEW. The important absorption bands occur at 1.48, 1.95, 3.0, 4.7 and 6.1 μ respectively.

SELENITE ($CaSO_4 + 2H_2O$).

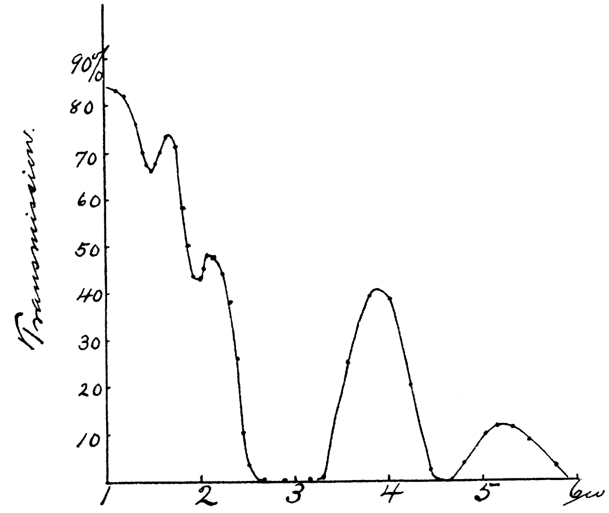

Fig. 2. Selenite. $t = .648$ mm.; water $= .318$ mm.

The transmission spectrum of a specimen of selenite 0.648 mm. in thickness, is given in Fig. 2. Since 21 per cent. of selenite is water, the thickness of the water if free would be 0.318 mm. (sp. gr. of selenite is 2.33). The specimen is transparent to 6 μ, while a layer of water 0.31 mm. is already opaque at 2.5 μ. The density of the water in selenite is so reduced that the absorption is only about one sixth to one tenth as great, see Fig. 1, curve b. For other thinner specimens see previous papers just quoted.

Tremolite, $CaMg(SiO_3)_4$.

The specimen of tremolite was quite transparent. The transmission of a section 0.23 mm. in thickness is given in curve *a*, Fig. 3. The equivalent layer of water would be 0.0138 mm. It is evident from this and from the transmission of a layer of water .014 mm. (Fig. 1), that the water in this mineral behaves like a highly attenuated vapor. No absorption bands of water are visible, the small bands which are present being common to silicates. In curve *b* is shown the transmission of a dehydrated specimen of tremolite .015 mm. in thickness. It was an opaque white mass and the increase in transmission with wave-length is no doubt due to the decrease in the scattering of the incident energy.

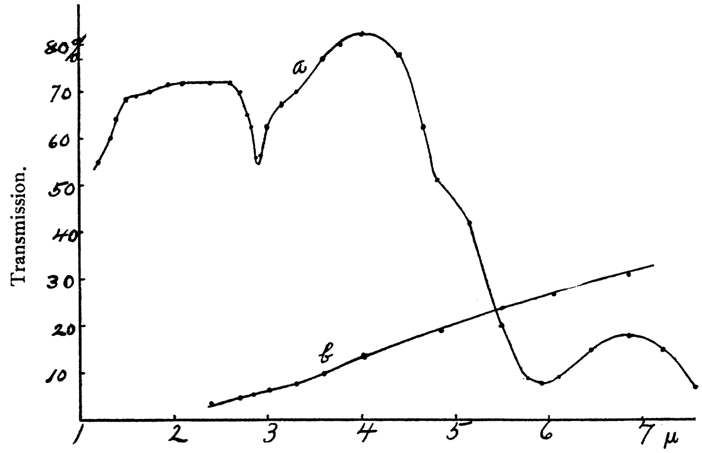

Fig. 3. Tremolite. $t = .23$ mm. Curve b, dehydrated specimen, $t = .015$ mm.

Muscovite Mica, $H_2KAl_3(SiO_4)_3$.

The transmission spectra are given in Fig. 4. Curve *a* was obtained with a rock salt prism, while curves *b* and *c* were observed with a fluorite prism. The thickness was .04 mm. Curve *b* shows the transmission of the specimen after dehydration. The absorption bands are common to silicates; and none are in common with those of water. The band of selective reflection beyond 9 μ does not seem to be affected by the constitutional water. The other bands disappear on dehydration, as they should, since on dehydration a new compound is formed — or rather, as in this case, only the constituent oxides remain. The layer of mica is too thin to show the weak absorption band of silica at 2.9 μ.

In conclusion it may be added that in substances (whether solid solutions or crystals) containing 7 per cent. of water the water bands were easily detected spectroradiometrically. But when the water content falls as low as 2 to 3 per cent. of the total weight of the substance, then the conditions which obtain in water vapor are found, and in the thin sections investigated the water bands are not detectable. The question then remains unexplained why a crystal containing water, and a solid solution of the same, show the absorption bands of water when other tests indicate that the crystal is a definite compound instead of discrete molecules of the substance cemented together with a definite amount of water.

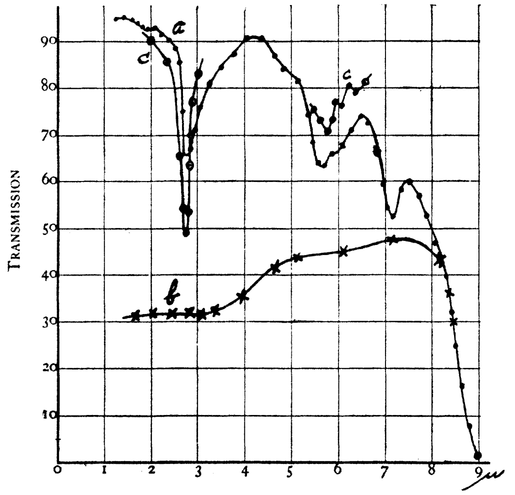

Fig. 4. Muscovite mica. Curve b, the same after dehydration ; $t = .04$ mm.

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