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Infra-Red Spectrum of Garnets

REGULARITIES in the infra-red absorption spectra of silicate minerals have been pointed out by Launer¹. Very recently, a much more detailed study of the strong absorption of the garnets in the 800–1,000 cm^{-1} range has been published by Wickersheim *et al.*². My results in this field extend down to 280 cm^{-1} and may be summarized as follows.

(1) If titaniferous garnets are excepted, the general infra-red pattern is pretty uniform, irrespective of the nature of the trivalent and bivalent cations. This pattern is highly characteristic of the garnets, and has not been observed in more than a hundred other silicates so far investigated³.

(2) The nearly linear relationship between the frequency ν of a given band and the length of the cell edge a_0 , mentioned by Wickersheim² is verified for all the bands down to 500 cm^{-1} ; it does not hold, however, for the bands observed at low frequencies. This is readily explained by the fact that most of these low-frequency bands are related to metal-oxygen vibrations, their position being chiefly determined by the nature of the cation itself.

On the other hand, it should be pointed out that, for certain bands at least, the slope of the straight line ν versus a_0 is slightly but definitely different for the two principal families of garnets, namely, the pyralspite and the ugrandite series.

(3) Garnets of the pyralspite family always exhibit one or two bands of low or medium intensity in the 350–280 cm^{-1} range. These bands are either missing or extremely weak for the garnets of the ugrandite family. This is reasonably explained if these bands are assigned to metal-oxygen vibrations of the bivalent cation (Fe II, Mn II, Mg) in eight-fold co-ordination: in the ugrandite garnets, this cation is mainly calcium, and the ionic bonds Ca—O should not give rise to discrete infra-red absorption bands.

(4) Some details may be characteristic of a given type of garnet. The discussion of such details is out of place here, and will be given in a forthcoming paper.

(5) In titaniferous garnets of the melanite-schorlomite-ivaarite series, the general infra-red pattern is more or less altered, the degree of alteration being roughly proportional to the amount of titanium. In these garnets, titanium is in four-fold co-ordination (at least partly), and thus replaces silicon. This

assignment has been discussed at length in a previous paper⁴.

From a more theoretical point of view, the most important feature is the uniformity of the bands assigned to SiO_4 fundamental frequencies. This uniformity is somewhat surprising, as $R^{\text{III}}\text{O}_6$ octahedra and $R^{\text{II}}\text{O}_6$ dodecahedra are the nearest neighbours of the SiO_4 tetrahedra, and partial isomorphic replacement of either R^{III} or R^{II} (which always occurs in garnets) should alter the local symmetry around the SiO_4 group.

This is in contrast with the strong influence of the introduction of TiO_4 tetrahedra in the structure. This introduction does alter the infra-red pattern of the SiO_4 tetrahedra, although the TiO_4 and SiO_4 are not mutually linked.

This interesting behaviour is not restricted to the garnet type, and has been observed in other series of isomorphic orthosilicates⁵.

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BIOCHEMISTRY

Vitamin A₁ Aldehyde in Hen's Eggs

WE have recently reported¹ that vitamin A₁ aldehyde occurs in the ripe eggs of several marine teleost fishes, and is the predominant form of vitamin A in them. In that paper we stated that we could not detect vitamin A₁ aldehyde in hen's eggs, but further experiments have shown it to be present.

Eggs from inseminated Light Sussex hens on a breeder's mash containing 2.4 mgm./kgm. of pre-formed vitamin A were used, the eggs being stored at 4°C. until used. The yolk was separated from the white, and extracted as previously described for fish eggs¹. When the extract was subjected to gradient elution chromatography², with a large column to take 2 gm. of lipid, the fractions that might be expected to contain vitamin A₁ aldehyde gave in the Carr-Price test only a fleeting blue colour, which soon became reddish-brown. Ultra-violet absorption curves gave no definite proof of the presence of aldehyde. However, when these fractions were reduced with sodium borohydride and the product subjected to chromatography by a modification³ of the method of Thompson, Ganguly and Kon³, vitamin A₁ alcohol was found by the Carr-Price test to be present, and was presumably derived from vitamin A₁ aldehyde in the original extract, the calculated amount being about 11 μgm . in the whole yolk. The other lipid material in the fractions apparently interfered with the direct characterization of the aldehyde.

In herring eggs, the vitamin A₁ aldehyde is bound to a lipid and, either directly or indirectly, to protein¹. If it were so in the yolk of hen's eggs, then by first extracting the lipids with a fat solvent without denaturing the proteins, and then denaturing them and extracting again, it might be possible to separate the aldehyde from most of the lipid. To test this possibility, each of several yolks was freeze-dried, ground to a powder and extracted with diethyl ether