

Infra-red Spectra of High-temperature Phases of Kaolinite and Halloysite

KAOLINITE and halloysite in the temperature-range 650–900° C. do not show any pronounced X-ray interference. In this range metakaolinite is formed; its Si—O hexagonal network remains more or less unchanged, while the octahedral sheet is deformed in absence of OH-groups^{1,2}. In kaolinite and halloysite, dehydration brings about a random arrangement in the direction of the *c*-axis. In pure and perfectly crystallized kaolinite, heated in the differential thermal apparatus at a velocity of 10 deg. C. per min. just above the exothermal maximum, X-ray examination reveals $\gamma\text{Al}_2\text{O}_3$ and mullite, whereas in halloysite only γ -alumina appears. In halloysite heated in the same way, mullite is observed³ only above 1,100° C. As the X-ray diagrams of mullite and sillimanite resemble each other closely, it is not certain which of these two phases is formed during the heating of kaolinite and halloysite.

Examination by infra-red radiation, however, seems to throw more light on the structure and enables a better identification of these phases.

We have studied the infra-red spectra (in the range $\lambda = 2\text{--}15\mu$) of the high-temperature phases of a pure and well-crystallized kaolinite from Škočaj (Croatia) and a pure halloysite from Gradešnica (Macedonia), in 'Nujol' and potassium bromide respectively. Fractions less than 2μ thick were used for examination, while the products of heating were obtained in a differential thermal apparatus at a heating velocity of 10 deg. C. per min.

Infra-red spectra of the kaolinite, between 8.7 and 10.4 μ , show four absorption bands with maxima at 9.1, 9.3, 9.6 and 9.9 μ which can be ascribed to the Si—O linkage, octahedral alumina sheet giving an absorption band with maximum at 10.9 μ , whereas the absorption band at 2.7 μ belongs to OH-radicals bound in the octahedral sheet⁴. In the metakaolinite range, the products of heating no longer show the absorption band at 10.9 μ (indicating the complete dislocation of the octahedral sheet) or at 2.7 μ (indicating absence of OH-groups). In the same samples left in the open for 20 days, no bands of adsorbed water at 3–4 μ and 6 μ could be observed. In metakaolinite, absorption bands of kaolinite between 8.7 and 10.4 μ are replaced by a wider band between 7.9 and 10.5 μ which, as regards the absorption bands of kaolinite, is shifted towards shorter wave-lengths. This band is considerably narrower and at a shorter wave-length as compared with the corresponding absorption band of aluminium-silica gel of the same composition heated at the same temperature. This suggests a greater order in the Si—O sheet. The decomposition of metakaolinite is accompanied by an increase and widening of the same absorption band which becomes less and less pronounced because of the intensified absorption in the range 10–15 μ . Infra-red spectra of the products heated at 1,200–1,350° C. are more like those of mullite than of sillimanite⁵.

It can be shown by the infra-red spectra that there are some essential differences in the properties of the high-temperature phases of kaolinite and halloysite, specially in the X-ray amorphous metakaolinite range. The infra-red spectrum of the halloysite examined shows the absorption band of the octahedral alumina sheet with a maximum at 10.9 μ , Si—O maximum at 9.6 μ , a maximum at 2.92 μ (H_2O in interlayers), and a maximum at 2.75 μ (OH-groups

in the octahedral sheet). The products of heating halloysite in the metakaolinite range no longer show the absorption band with a maximum at 10.9 μ ; the absorption band of the Si—O linkage is, in this case, wider than the corresponding absorption band of kaolinite heated to the same temperature. It already becomes less pronounced in the metakaolinite range (above 700° C.) owing to the intensified absorption in the range 10–15 μ . After crystallization of $\gamma\text{Al}_2\text{O}_3$ in the range of exothermal maximum, the Si—O linkage becomes more pronounced, with a maximum at 9.1 μ . As in kaolinite, the infra-red spectra of the products of heating halloysite between 1,200° and 1,350° C. are more like the infra-red spectra of mullite than those of sillimanite.

The differences between kaolinite and halloysite in the metakaolinite range regarding the absorption bands of bound and free OH-groups are of special interest. The products of dehydration of halloysite in the range of 650–850° C., unlike those of kaolinite, are very hygroscopic, showing an absorption band between 2.5 and 3.5 μ with a maximum at 2.95 μ , as well as an absorption maximum at 6.15 μ . Taking certain precautions, we have succeeded in protecting the products obtained at 680° and 720° C. (proved amorphous by X-rays) from humidity, so that the infra-red spectra obtained showed a very poor absorption band at 6.15 μ , while the large band between 2.5 and 3.5 μ was split into two smaller bands with the maxima at 2.95 and 2.71 μ . While the occurrence of the bands at 6.15 and 2.95 μ can be assigned to adsorbed water, the band at 2.71 μ suggests free OH-groups probably bound to AlO-groups. It appears very likely that the crystallization nuclei of $\gamma\text{Al}_2\text{O}_3$ are already formed in the metakaolinite range, and that their formation is enhanced by the retarded OH-groups, which have a stabilizing effect on that compound⁶.

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Density of Marine Benthic Communities off West Africa

RECENTLY, Thorson¹ has suggested that a series of related marine benthic communities might occur on level sea-bottoms from the Arctic to the tropics, similar communities occurring on similar deposits irrespective of latitude, and he directed attention to the possibility of studying, in these communities, growth-rates and recruitment of stock under similar ecological conditions in cold and in warm seas.