552. 52 : 542. 6 : 53. 082. 5

Anomalous Phenomena on Refractive Indices of a Clay Mineral Measured by Immersion Method.

By

Osamu Hirokawa

Introduction. In the course of writer's study of building stone, he found that a clay mineral which makes the greater part of the so-called "Miso" in the Ôya-ishi, a tuffaceous building stone, presents anomalous phenomena on the refractive indices measured in some immersion liquids. Since these phenomena seem to be of special notice to the writer not only from the view point of academic interests, but also from the practical application, a short note with regards to the results of his experiments and observations will be given in this paper. It is, of course, not necessary to say that the further study is desirable to develop the problems. This paper is merely a step to this development.

Mineralogical description. "Miso" is of angular form, 0.5 mm ~ 1 cm in size, showing sharp boundary against the country rock and composed of the clay mineral besides bipyramidal quartz constituents plagioclase (oligoclase — andesine), zeolite (?) and zircon, as accessory constituents. The clay mineral is various in both colour and composition. A yellowish white variety is now in question in the following.

Under the microscope, the clay mineral appears as a sheaf of rods and tubes, 0.15 ~ 0.03 mm across showing weak birefringence. The rod and tube are constituted of aggregate of cilia, which crowd at random. The suspensoid, consisting of the mineral and water, is about 7 in pH. This mineral is characterized by swelling and synersis in both of acid and alkaline water.

Experimental results of ignition loss and chemical composition of the mineral are given in Table I and Table II.

From these characters this mineral seems to be beidellite, a variety of montmorillonite.

Experiment and observation. The writer has discovered that the mineral[1] is lower in indices of refraction than cedarwood oil (n = 1.523), but it appears as if it were higher in indices of refraction than the mixed liquid (n = 1.528) of cedarwood oil and cassia oil (n = 1.602). Some results of this experiments and observations in connection with this discovery are as follows:

In the mixed liquid (n = 1.545) of these two, the mineral appears, as if it were about the same in refractive index as the liquid. It is, however, of special notice to find that the mineral behaves to become higher in refractive indices than the liquid during measurement.

Being measured in the other mixed liquid, which has higher index of refraction, the mineral is lower in indices of refraction than the liquid at first, but some flakes of the mineral begin to behave, as if they were higher in indices of refraction than the liquid during experiment. This change of optical character takes place more rapidly, as the flake of the mineral is smaller.

In the same way, the mineral appears, as if it were higher in indices of refraction than the mixed liquids (n = 1.523 and 1.557) of ethyl benzoate (n = 1.1510), and cassia oil (n = 1.602).

In the mixed liquids (n = 1.523) of α-chlornaphthalene (n = 1.640) and cedarwood oil or ethyl benzoate, the mineral is always lower in indices of refraction than the liquids.

The mineral, immersed in cassia oil, cedarwood oil and the mixed liquid (n = 1.528) of these two[2], for 24 hours, shows similar phenomena, as described before.

1) The refractive indices of this mineral means α and γ in this paper.

2) The refractive indices of these three liquid show no remarkable change after 24 hours.

It shows still the same phenomena on refractive indices measured by immersion method, after the mineral is heated at 100°C and dehydrated.

In ethyl henzoate (n=1.510), benzol (n =1.505) or petroleum (n=1.434), the mineral which has absorbed water, appears as if it were lower in indices of refraction than the liquids, while the mineral dried in the air is higher in indices of refraction than these three oils.

The mineral which has absorbed water is expected to be lower in indices of refraction than glycerine (n=1.463), but it appears as if it were higher.

Arguments. It has been reported that the refractive indices of clay mineral as haloysite shows remarkable change by the water content of the mineral, and in some cases the change of refractive indices are probably due to the subtraction of water from the mineral by some immersion liquids during measurement[3].

The mineral in question contains a large quantity of water, being characterized by swelling and synersis. Therefore, some changes of refractive indices of the mineral, especially in the case of the mineral which has absorbed water, seem to be in connection with the change of the water content. But the main facts above-mentioned are difficult to follow this theory.

It seems to be probable to the present writer that the anomalous phenomena are due to the formation of jelly[4]-like substance by selective sorption of the immersion liquids by the mineral. For instance, the sorption of cassia oil by the mineral is more remarkable in the mixed immersion liquid of cedarwood and cassia oils, the latter oil diffusing into the mineral to form jelly-like substance, which is higher in indices of refraction than the mixed liquid. Furthermore, the writer is inclined to consider that the sorption of α-chlornaphthalene by the mineral is not so remarkable, resulting no marked anomaly in the refractive indices of the mineral in any of the mixed liquids of α-chlornaphthalene and the other oils.

It is possible too that the jelly-like substance, formed through sorption of water by the mineral, has consequently lower indices of refraction than the immersion liquids like benzol, petroelum etc. While glycerine forms easily a mixture with water, the jelly-like substance consisting of water and the mineral appears, therefore, as if it were higher in indices of refraction than the glycerine.

What the present writer says in the forgoing pages is of importance, when the refractive indices of the minerals, which are liable to give rise to sorption are tried to be determined by immersion method. It is necessary to pay attention to the water content of the minerals and to use unmixed liquids, which show no affinity with water.

The refractive indices of the mineral, now under consideration, when dried in the air, are between the refractive index of ethyl benzoate (n=1.510) and cedarwood oil (n=1.523), so far as the immersion method is used here to determine them.

This interpretative result is merely based on the insufficient experiments and observations. There is, therefore, no doubt that further experiments and observations on this problem are very desirable.

15 th, June, 1949.

Table I (after Takeshi Ando)

SiO	49.66
Al_2O_3	17.96
Fe_2O_3	2.87
FeO	0.37
MgO	2.02
CaO	2.01
Na_2O	0.32
K_2O	0.54
H_2O (+)	6.21
H_2O (−)	17.95
TiO_2	0.13
MnO	0.55
P_2O_5	0.02
Total	100.10

Table II (after Kiyoo Kawada)

Temperature (°C)	Loss of wt. %
40	2.93
50	9.70
70	16.58
90	17.08

3) These phenomena have been well studied by C. E. Marshall; G. Nagelschmidt; C. S. W. Correns; M. Mehmel etc.

4) Jitsusaburo Samejima: Colloid 1938

100	17.34
110	17.37
120	17.48
130	17.98
150	18.55
170	18.55
190	18.57
210	18.57
230	18.84
300	18.87
350	18.95
380	19.18
400	19.32
450	19.52
500	19.64
600	20.83
700	21.71

或る種の粘土鑛物の屈折率を浸液法により測定する際見られる異常現象

広　川　治

要旨

大谷石の中に，所謂「みそ」と称する部分がある。このものは鉱物学的にはモンモリロナイトの一種と考えられるが，著者は浸液法によつてその屈折率を測定中，興味ある異常現象の見られるのに気が付いたので，それについて簡単に述べる。

(1) 大谷石中の所謂「みそ」は，屈折率の値が cedarwood oil (n=1.523) よりも低い。然るに cedarwood oil と cassia oil (n=1.602) の混合液の中でベッケ線の動きを観察すると，次の如き現象が見られる。

(2) cassia oil 及び cedarwood oil の両液を混合して得られた液 (n=1.528) の中では，液よりも鉱物の方が屈折率に於て高いかの如く観察される。今 cassia oil の量を増加し，高い屈折率(n=1.545)の混合液を作り，その中で観察すると，初めの中ベッケ線は稍々不明瞭であるが，測定中に鉱物の屈折率が浸液よりも高くなつたかのような動きを示してくる。更に cassia oil の量の多い浸液中では，初めの中は浸液よりも鉱物の屈折率が低いが，測定中に，細粉の或るものゝ屈折率は浸液の屈折率よりも高くなつたかの如く観察される。この場合，鉱物粒が小さい程このような変化は速かに行われ，又，混合液中の cassia oil の量が多い程この変化が行われるのに時間を要する。

(3) ethyl benzoate (n=1.510) と cassia oil (n=1.602) とを用い二種の混合液 (n=1.523 及び 1.557) を作り，その中で観察すると，ベッケ線の動きは何れの浸液よりも鉱物の屈折率が高いかのようにあらわれる。

(4) α-chlornaphthalene (n=1.640) と cedarwood oil 又は ethyl benzoate との混合液 (n=1.523 以上) より，鉱物の屈折率は常に低い。

(5) cassia oil, cedarwood oil 及びその混合液の中に鉱物を一晝夜放置した後，鏡下で観察した場合にも，同じ現象が見られ，三種の液の屈折率には殆んど変化がなかつた。

(6) 鉱物を温度 100°C に加熱し，脱水を行つた後上述の実験をくりかえしたが，此の場合にも同じ結果が得られた。

(7) 鉱物に水を吸収させて ethyl benzoate (n=1.510) benzol (n=1.505) 及び petroleum (n=1.434) 中に浸して観察した。この場合，ベッケ線は，鉱物が何れの浸液よりも低いかの如くあらわれる。しかし普通の乾燥状態で水を吸収させない場合には，鉱物は上述の三種の油の何れよりも屈折率が高い。

(8) 次に glycerine (n=1.463) を浸液としてその中に水を吸収させた鉱物を入れた場合には，水を吸収させなかつた場合と同じく，屈折率に於て，鉱物の方が高いようにベッケ線は現われる。

(9) 以上の観察並に実験は一應次のような理論に集約することが出来る。即ち鉱物と浸液との間に選択的な收着が行われる結果，一種の凝膠体というべきものが形成されると考える。そうすると收着が進むと共に凝膠体の屈折率は変化し，收着が充分行われたとき，凝膠体の屈折率は最大又は最小に達する。この場合液が收着され始めてから平衡に達する迄の凝膠体の屈折率は，收着された液の屈折率と，鉱物の屈折率の間の値を有するものであろう。

(10) 以上の事柄を実用的立場から結論すると，收着現象を生ずるような物質の屈折率を浸液法で測定する場合には，その物質中の水分含有量に注意し，水と混和しないような純粋の液体を用いて決定しなければならないことがわかる。なお純粋の液体である ethyl benzoate 及び cedarwood oil を用い，普通の乾燥状態に於て問題の鉱物の屈折率を測定した結果は，$\alpha > 1.510$, $\gamma < 1.523$ である。