

CLAYS AND OTHER MINERALS FROM THE DEEP SEA, HOT SPRINGS, AND WEATHERED ROCKS.

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ABSTRACT.

X-rays and optical methods were used. Comparison materials, especially clays, required study. It was found desirable in the nomenclature of the optical properties of clays to take account of the differences in aggregate refractive indices observed for most clays when differently immersed. Staining was used to indicate the presence and the character of clays.

Some of the minerals observed in the bottom samples taken by the *Carnegie* were: dolomite, considered syngenetic; muscovite, considered residual; montmorillonite and phillipsite, syngenetic; and one unidentified iron-manganese mineral.

Some constituents of the samples described in this paper were identified petrographically, others by means of X-ray powder patterns.

Deposits may contain dispersed clay which, if the sample is dried, adheres to the larger grains. An informative separation before drying can be made rapidly by taking up a little of the deposit with water in a medicine dropper, then as successively finer portions settle, depositing them as separate droplets on a slide. These may be dried, or the finer portions may be examined wet. The search for clays in deposits is expedited by applying stains, as described below.

CLAYS.

Petrographic Examination of Clays.

The optical properties of some clay minerals appearing in determinative tables are those of indefinite porous aggregates for which a numerical value as obtained by the immersion method may represent a sum or combination of effects due chiefly to the stable part of the clay mineral, and to the immersion liquid which has replaced part of the loosely held water and has partly filled the pores. A symbol is needed to indicate such indefiniteness in case of aggregates of various kinds. *Sigma* might be used as a subscript: $n_{\Sigma} = 1.48$, $n = 1.48_{\Sigma}$, $(\gamma - \beta)_{\Sigma} = 0.03$, etc. The designations *aggregate refractive index* and *aggregate birefringence* for these quantities may be

found acceptable. Such numerical values, although indefinite, are essential for comparative studies, and are being made more definite.

Delayed or non-uniform penetration of immersion liquids into porous aggregates has been a source of much uncertainty.¹ Correns and Mehmel² have used for clays a mixture of quinoline and paraldehyde which gave for montmorillonite a maximum refractive index in about two and a half hours. We have observed that the refractive index of this liquid increases rapidly with exposure on a slide, but a test of the rate of its effect on clays for the first few minutes of immersion was made on several beidellites and montmorillonites in grains only a few microns thick. In all cases the aggregate refractive index of many of the grains exceeded 1.572 in less than two minutes (see below). Kaolinite, halloysite and halloysite-hydrate fall below this. In early determinations,³ when slowly penetrating heavy petroleum or fatty oils were used for immersion, the observed refractive indices of beidellite and montmorillonite were usually much lower than those of kaolinite. Whether or not quinoline and paraldehyde penetrate disproportionately is not known.

Aniline is a most rapidly penetrating single liquid of suitable refractive index for the microscopical study of clays. Around a little heap of montmorillonite powder immersed in it an emulsion of the expelled water was seen to form. A lump thus immersed had its displaced water driven at once to the interior. Then by slow diffusion the water escaped, causing a decrease in aggregate birefringence from four to two orders of interference, and an increase in the aggregate refractive index. Aniline (b. p. 183°) mixed with a little iso-amyl iso-valerate (b. p. 194°) and also the quinoline-paraldehyde mixture were used to test the homogeneity of several compact beidellites and montmorillonites. Thin shavings of the clays developed birefringent streaks parallel to the knife edge. For liquids of refractive index 1.57 there were great differences in the rate of penetration for these clays from different localities, but the quinoline liquid was more quickly effective.

¹ Sosman, R. B., Hostetter, J. C., and Merwin, H. E.: *J. Wash. Acad. Sci.*, 5, 565, 1915; Johnston, J., Merwin, H. E., and Williamson, E. D.: *This Journal*, 41, 482, 1916; Larsen, E. S., and Wherry, E. T.: *J. Wash. Acad. Sci.*, 7, 179 and 209, 1917.

² Correns, C. W., and Mehmel, M.: *Z. Krist.*, 94, 337, 1936.

³ Shannon, E. V.: *U. S. Nat. Museum Bull.*, 131, 388, 1926; Ross, C. S., and Shannon, E. V.: *J. Am. Ceram. Soc.*, 9, 94, 1926.

The birefringence in water of two of these clays (Nos. 2 and 4 of Table I) was estimated on coherent grains as 0.02₅.

In complex deposits, the clay—and some other porous substances—can be stained by having a little safranine, crystal violet, or malachite green in the immersion liquid. If the grains are tinted at room temperature no significant immediate effect of the dye on refractive index has been observed, but by boiling for two minutes montmorillonite, beidellite, halloysite,⁴ halloysite-hydrate,⁴ and the very fine-grained kaolinite⁴ (impure?), indianite, in aniline or anethole containing sufficient safranine, the aggregate refractive indices were raised 0.02 to 0.03 by the dye.

X-ray Examination of Clays.

Most of our comparisons of X-ray powder spectra were made by having a known and an unknown clay pattern on one film. Beidellites and montmorillonites were all very similar except for slight differences in spacings and a few extraneous lines. There was a general tendency for all spacings of one clay to be shifted in the same direction with respect to another clay. Therefore we list in Table I the clays in the order in which their interplanar spacings increase. This table also describes the occurrence of the specimens.

TABLE I.

Order of Interplanar Spacings of Clays.

1. Hillside Springs specimen. It occurred in a rhyolite altered by hot water in Yellowstone Park (see ref. 7). It is probably a very pure aluminum beidellite.
 2. Beidellite from Silver City (Carson District). It contains a little CaO (2.76%)—see ref. 3.
 3. Beidellite from "The Geysers."^a It is a green clay containing about 6% Cr₂O₃ and 2% Fe₂O₃, according to a partial analysis of another part of the specimen.
 4. Beidellite from Colorado.^b This is a specimen containing about 9% Fe₂O₃, and 3% CaO.
 5. Light-colored clay from the deep sea nodule, as described below.
 6. Otaylite.^c This is a montmorillonite containing about 8% MgO and 1% CaO, besides 3% Fe₂O₃.
 7. Dark clay from the deep sea nodule, as described below.
 8. Clays from *Carnegie* samples, Nos. 27, 61, and 80. (See Table II.)
- ^a Allen, E. T., and Day, A. L.: *Carnegie Inst. Wash. Pub. No. 378*, p. 49, 1927.
- ^b See Ross and Shannon, ref. 3, and also the first reference under c, below.
- ^c See X-ray diffraction, Hendricks, S. B., and Fry, W. H.: *Soil Sci.*, 29, 457, 1930; and Lauder milk, J. D., and Woodford, A. O.: *Am. Mineral.*, 19, 260, 1934.

⁴ Samples of the halloysites kindly furnished by Dr. S. B. Hendricks. See *Am. Mineral.*, 23, 295, 1938.

ALTERED PUMICE FROM A DEEP SEA BOTTOM SAMPLE
TAKEN BY THE *Carnegie*.⁵

Cross sections of a black nodule one to two centimeters in diameter, from a bottom sample at 5,396 meters depth 200 miles off the coast of Japan, showed irregular color banding from the black surface through a dark brown zone and a buff zone to a white pumiceous interior.

The refractive index of the isotropic pumice was 1.513, except that the largest inter-bubble fragments had a noticeably lower refractivity at the center, as though increase of refractivity by hydration⁶ had been taking place. Glass gave way irregularly, as if by solution, to secondary products without notable pseudomorphic replacement. Near the center of the nodules, bubble cavities were partly filled with a light-colored, decidedly birefringent, unconsolidated clay. Toward the surface, the clay became less birefringent, browner, and denser. The birefringent elements appeared both felted and spherulitic. The *aggregate refractive index* obtained by immersion in aniline mixtures (from less than 1.58 to greater than 1.63) increased with the color toward the surface. The more consolidated darker material just within the surface below the black crusts was nearly isotropic, often with a concentric or irregular layering, and had an aggregate refractive index much higher than 1.63. X-ray spectrograms of the light and dark portions both showed lines characteristic of montmorillonite and beidellite. The interplanar spacings were smaller for the light portion (see Table I).

The black crust of the nodules less than one millimeter thick was minutely botryoidal and contained, besides the main dark brown constituent, small amounts of quartz and montmorillonite. An X-ray powder photograph showed three strong broad lines regarded as characteristic at 2.43, 1.42, and 1.23 Å. The same lines were obtained from five other sources: (1) solid manganese nodules in *Carnegie* bottom sample No. 79 at a depth of 4,918 meters; (2) minute black particles magnetically concentrated from *Carnegie* bottom sample No. 80, depth of 5,003 meters; (3) a weathered manganeseiferous travertine collected by

⁵ This sample (No. 57) and those described later (see Table II) were kindly placed at our disposal by J. S. Fleming, Director, Department of Terrestrial Magnetism, Carnegie Institution of Washington.

⁶ Fresh volcanic glasses containing water have higher refractivity than anhydrous ones of otherwise corresponding composition. Tilley, C. E.: *Mineralog. Mag.*, 19, 294, 1922.

Allen⁷ in Yellowstone Park; (4) a black deposit in Firehole Pool, also collected by Allen⁷ in Yellowstone Park and analyzed chemically; (5) a dark brown coating on grains of manganese carbonate from an open bottle that had been standing on a laboratory shelf for several years. All these materials are essentially oxides of iron and manganese, in part hydrated. Therefore powder patterns of them were compared with those of known minerals⁸ of related composition. The results, however, were negative.

SOME MINERALS IN THE SEA BOTTOM SAMPLES
COLLECTED BY THE *Carnegie*.⁹

One highly calcareous sample (No. 21) was treated with dilute citric acid to remove the shells without decomposing the little dark brown globules that had been observed within them. The residual globules were sensibly isotropic with an *aggregate refractive index* of 1.8. The tiny sample was X-rayed, but no identity with a known substance was established. The approximate positions of the lines are listed here, and the stronger ones are italicized: 4.2, 2.7, 2.45, 2.11, 1.71, 1.50, and 1.42 Å. Microscopically this material appears to be like scattered grains five to fifteen microns in diameter found in red clays of the deep ocean.

Dolomite was found in separate microscopic rhombohedra in the following bottom samples: Nos. 29, 62, 64, 65, and 85, from widely separated localities in the Pacific. It would seem not a long step to syngenetic dolomites by direct sedimentation.

In a very fine mud in mid-ocean west of Mexico (sample No. 77), the largest grains were flakes resembling muscovite. By means of X-rays, *muscovite*, *quartz*, and *phillipsite* were found. Derivation from the granitic and metamorphic rocks of western North America is inferred.

Phillipsite, as single or grouped prisms, is often obscured by adherent mud, but it has long been known as a constituent of deep sea deposits. Its birefringence may be very weak even in large zoned crystals. The refractive index is slightly variable

⁷ Allen, E. T., and Day, A. L.: Hot Springs of the Yellowstone Park, Carnegie Inst. Wash. Pub. No. 466, pp. 346, 348, 1935.

⁸ Furnished by the U. S. National Museum through the kindness of Dr. W. F. Foshag. Polionite, R. 2096, and pyrolusite, 86237 (both gave patterns like synthetic MnO₂); nsilomelane, 93687; manganite, 82428; braunite, 45375; pyrochroite, R. 2208.

⁹ Minerals not mentioned should not be considered absent. See Table II for locations.

(around 1.495). Outlines of grains may be seen in samples of undried mud taken from filter paper to aniline or quinoline.

Montmorillonite with large interplanar spacings like those of the dark clay of the black nodule was found by X-rays in Nos. 27, 61, and 80. Quartz also was present, and phillipsite in Nos. 27 and 61.

A BOEHMITE SOIL.

A "red" residual soil was collected by T. W. Vaughan from the limestone of the Anguilla formation on the Island of Anguilla. It consists of pellets of various sizes, some decidedly spherulitic, which have an aggregate refractive index of 1.62 to 1.64 and are very birefringent. All are peppered with minute grains having both very high refractive index and very high birefringence. The grains probably are titanium oxide. Hematite appears in small grains, some of which are spherulitic. Quartz grains are present but not abundant. X-ray examination shows abundant boehmite, little hematite and quartz, and kaolinite, probably. Stains color the pellets unevenly, but tests on artificial boehmite show that it is porous enough to stain decidedly.

TABLE II.

Location and Depth of <i>Carnegie</i> Bottom Samples.				
Sample No.	Lat.	Long.	Depth meters	Approximate location
21	33 59 S.	106 43 W.	3139	2000 miles W. of Valparaiso
27	31 54 S.	88 17 W.	3879	1000 miles W. of Valparaiso
29	24 57 S.	82 15 W.	1089	700 miles W. of Northern Chile
57	37 40 N.	145 26 E.	5396	200 miles off the coast of Japan
61	44 16 N.	137 37 W.	4081	600 miles W. of Oregon
62	40 37 N.	132 23 W.	3785	400 miles W. of Oregon
64	33 49 N.	126 20 W.	4418	400 miles W. of Los Angeles
65	31 38 N.	128 48 W.	4251	1000 miles W. of Los Angeles
77	21 18 N.	138 36 W.	5320	Mid-ocean between Hawaii and Lower California
79	12 40 N.	137 32 W.	4918	Mid-ocean between Hawaii and Panama
80	7 45 N.	141 24 W.	5003	Mid-Pacific west of Panama
85	10 54 S.	161 53 W.	2614	East of Samoa