HIGH-ALUMINA ALLOPHANE AS A WEATHERING PRODUCT OF PLAGIOCLASE

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Abstract

Allophane with an exceptionally high content of alumina occurs in granodiorite in the northwest part of the Bass Lake quadrangle, Mariposa County, California. Chemical analysis of the mineral gives SiO_2 15.1, Al_2O_3 47.7, CaO 0.29, Na_2O 0.24, K_2O 0.14, H_2O^+ 20.8%, H_2O^- 15.7%, (alumina determined by difference), corresponding to the formula $SiO_2 \cdot 2Al_2O_3 \cdot 8H_2O$. The allophane is optically isotropic and is amorphous to infrared and X radiation. Occurrence as cores to plagioclase crystals suggests a secondary origin, and it is probable that development of allophane represents the first stage of weathering of the rock.

Introduction

During study of some Sierra Nevadan igneous and metamorphic rocks exposed in the northwest part of the Bass Lake quadrangle, Mariposa County, California (Snetsinger, 1965), transparent, isotropic material with low refractive index was seen in thin section as cores to plagioclase crystals in granitic rock. A very small amount of this material was purified from a sample of granodiorite, and X-ray and infrared study showed it was amorphous, suggesting allophane. A larger amount from the same sample was prepared for chemical work, but the analysis yielded a formula quite distinct from that usually found for allophane. Pertinent chemical and physical data are given below.

Petrographic Relations

The allophane makes up less than a percent of the granodiorite from which it was separated; major mineral content of this rock is quartz, 18%; plagioclase, 52%; potash feldspar, 12%; hornblende and biotite, 18%. Allophane occurs most commonly at the cores of plagioclase crystals, but thin, anastomosing veinlets may reach rims of grains, as illustrated in Figure 1.

Separatory Procedure

In order to free it from associated plagioclase, the allophane was finely ground and centrifuged in bromoform diluted with acetone. Its hydrous nature made air-drying necessary to prevent loss of water: at no point during purification was the material washed with water. A few brown-stained grains, present in the final pure fraction, were removed with the Frantz electromagnetic separator. Before analysis, the pure allophane

was washed repeatedly with acetone to eliminate bromoform, and then left to dry in air for two weeks at room temperature in a lightly covered dish so that (1) all acetone was evaporated and (2) any water extracted during acetone treatment was readsorbed. About 200 mg. of the mineral were obtained for analytical work.

ANALYTICAL PROCEDURE

Water loss at 110°C was determined by heating for 24 hours in an oven adjusted to $\pm 1°$ of that temperature, and total water was calculated as loss upon ignition at red heat to constant weight. Following ignition, the allophane was decomposed with HF and a little H_2SO_4 and silica deter-

FIG. 1. Mode of occurrence of high-alumina allophane. The isotropic core to the plagioclase crystal in the center of the field of view is allophane; the plagioclase grain is surrounded by grid-twinned potash feldspar. Crossed polarizers ×18.

mined by volatilization as SiF_4. The residue contained mainly Al_2O_3 with minor amounts of calcium and the alkalies. Alumina was calculated by difference after determination of all other oxides, a satisfactory procedure since the only other elements detected were barium and iron, and these were present in spectrographic traces.

NOMENCLATURE

The analysis of this mineral closely corresponds to that of a mineral which previous workers have called collyrite. Des Cloiseaux (1862), Dana (1885) and Doelter (1917) group collyrite with the clay minerals, and present several early analyses of it, the most recent of which was done over one hundred years ago. Analyses of optically isotropic clay minerals made prior to the advent of X rays are, however, open to question since such materials may have consisted of minutely crystalline clays or mixtures of clays. Indeed, Kerr and Hamilton (1949) reported

X-ray examination of a sample of collyrite indicated it was actually kaolinite, and they suggested that the name collyrite represents no definite mineral species, and should be dropped. Hey (1955) notes collyrite as a doubtful species and Rost (1944) has studied examples that proved to be mixtures of clays. Collyrite is not included in Brown's (1955) report on nomenclature of clay minerals. It appears that "collyrite" is not valid; at least, the name is not in recent usage. The mineral described in this report is therefore called "high-alumina allophane."

Examination of the literature on amorphous clay materials shows that these are, despite their noncrystalline nature, commonly referred to as minerals, and the usage is adopted here, although some might prefer the term "mineraloid."

Composition and Physical Properties

Chemical analysis of the allophane is given in Column (1) of Table 1. Alumina, water and silica are major constituents, and their molecular proportions suggest the approximate formula $SiO_2 \cdot 2Al_2O_3 \cdot 8H_2O$, which is in fair agreement with the four previous analyses of "collyrite" (Columns (2)–(5), Table 1). Analysis (5) is especially comparable to the present one, but analysis (4) is closer to normal allophane than "collyrite."

Mineralogists interested in clays commonly identify as allophane any isotropic material which does not diffract X rays, but the silica-alumina ratios for this mineral cover a considerable range. Ross and Kerr (1934) refer to twelve allophane analyses where the ratio varied from 0.74 to 1.98, about one-half being not far from 1.0. Birrell and Fieldes (1952) record three New Zealand soil clay allophanes, the silica-alumina ratios of which range from 1.01 to 1.78. Mitchell and Farmer (1962), studying two Scottish soil clays, found that when these contained a high percentage of allophane, ratios of 1.31 and 2.03 were obtained. The silica-alumina ratio for the high-alumina allophane is 0.32, and thus the mineral is compositionally quite distinct from normal allophane. On the other hand water content is similar to that of other allophanes: Ross and Kerr (1934) cite a range of 33.06 to 43.96 weight percent of this constituent in allophanes, comparable to the present analysis.

X-ray examination of the high-alumina allophane fails to reveal any crystalline phase, even after glycolation. Infrared absorption[1] (Fig. 2) further indicates the mineral is amorphous, because areas of strong absorption corresponding to well directed bonds are absent. A poorly defined absorption band occurs near the Al-O, Si-O stretching region (1000 cm^{-1}) and the band near 550 cm^{-1} is a harmonic of that vibration. No absorption line suggesting O-H bond development occurs; the broad

[1] 1.8 mg. allophane in 400 mg. KBr.

TABLE 1. CHEMICAL ANALYSES

	(1)	(2)	(3)	(4)	(5)
Chemical Analyses in Weight Percent					
SiO_2	15.1	14.0	15.0	23.3	14.49
Al_2O_3[1]	47.73	45.0	44.5	42.8	47.44
CaO	0.29				0.89
Na_2O	0.24				
K_2O	0.14				
CO_2					0.79
H_2O^+	20.8	42.0	40.5	34.7	36.39
H_2O^-	15.7				
Total	100.00	101.0	100.0	100.8	100.00
Molecular Proportions					
SiO_2	1.00	0.93	1.00	1.55	0.96
Al_2O_3	1.87	1.76	1.74	1.68	1.86
CaO	0.020				0.06
Na_2O	0.016				
K_2O	0.008				
CO_2					0.07
H_2O^+	4.61 ⎫	9.32	8.99	7.70	8.08
	⎬ 8.09				
H_2O^-	3.48 ⎭				

[1] High-alumina allophane, Bass Lake, Calif. Analyst, K. G. Snetsinger (alumina by difference); calcium by N. H. Suhr, Pennsylvania State University, (spectrography); potassium and sodium by C. O. Ingamells, Pennsylvania State University (flame photometry); Ba and Fe present in spectrographic traces.

[2] "Collyrite" (Klaproth, 1795).

[3] "Collyrite" (Berthier, 1817).

[4] "Collyrite" (Kersten, 1831).

[5] "Collyrite" (Gladstone and Gladstone, 1862).

For sources of the earlier analyses see Dana, 1885, p. 420.

band near 3440 cm⁻¹ is considered due to adsorbed water, as is the weak band at 1650 cm⁻¹. The peak at 2375 cm⁻¹ may possibly be attributed to atmospheric CO_2, but is more likely the result of slight instrument imbalance.

Owing to lack of material, differential thermal analysis could not be performed. Some data are, however, available regarding dehydration-rehydration behavior at different temperatures, and these are summarized in Table 2. At the end of 40 hours at nearly 100% humidity, the allophane sample used to determine H_2O^- rehydrated partially, regaining 64 per-

cent of the water it had lost. The same partially rehydrated material, heated to 190°C for five hours, lost an additional 13.3 percent of the weight of the original sample, but was not capable of being rehydrated after having been heated to that temperature: at the end of 16 hours, no increase in weight of the sample was noted. Upon ignition at red heat a further 7.5 percent H_2O was lost; water given off at this temperature could also not be readsorbed. Thus nearly 80 percent of the water in the mineral is given off at temperatures below 190°C, and this is in contrast to common allophane, which shows gradual water loss to over 800°C. (Ross and Kerr, 1934). Apparently water is less tightly bound to the high-alumina allophane than it is to common allophane. Non-rehydration
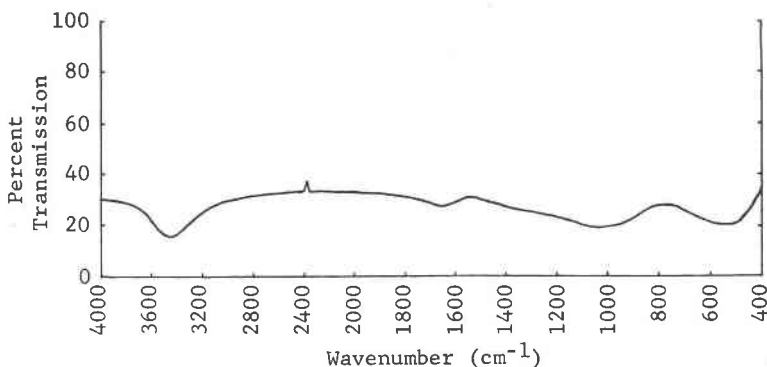

FIG. 2. Infrared absorption spectrum of high-alumina allophane.

after heating to 190°C is presumably the result of rearrangement of constituent molecular groups to positions that do not permit readsorption of water after heat treatment.

X-ray study of the ignited allophane failed to reveal presence of any crystalline phases. Heating for one hour at 1075°C, however, produced mullite, the cell dimensions of which[1] [a 7.58(4) ± 0.02 Å; b 7.70(6) ± 0.01 Å; c 2.880 ± 0.004 Å; cell volume = 168.3 ± 0.04 Å³] are near those of synthetic, iron-free mullite (Agrell and Smith, 1960). X-ray study showed mullite was the only crystalline phase formed at 1075°C.

This high-alumina allophane is considered to be hydrated amorphous alumina mixed with hydrated amorphous silica and minor bases. Water content is adsorbed, and it may in large part represent what Searle and Grimshaw (1959, p. 419) refer to as colloidal water, water needed to satisfy unsaturated charges on surfaces of colloidal particles. Molecular

[1] Obtained by the least squares computer refinement program devised by Evans *et al.* (1963).

proportions of major oxides present in this allophane are close to even numbers and it would be of interest to know if this is fortuitous or the result of balancing of charges on molecular groups. The writer has been unable, however, to decide the exact configurations of groups which may be involved and therefore charge relations remain uncertain.

Fully-hydrated (*i.e.*, untreated) material is isotropic, has a refractive index of 1.487 and a density of 2.10, ± 0.05 g/cc. Water is evolved in closed tube and the mineral is soluble in cold concentrated HCl. Loss of adsorbed water has an effect on refractive index and density: after heating for 15 minutes at 75°C, refractive index is raised to 1.51, ± 0.01 and, after ignition, refractive index and density are 1.53, ± 0.01 and 2.32, ± 0.05 g/cc. Study of grain concentrates shows that the mineral has a strong tendency of occurrence as large (0.1 mm) platelets.

TABLE 2. DEHYDRATION-REHYDRATION BEHAVIOR OF
HIGH-ALUMINA ALLOPHANE

Temperature	Percent H_2O loss	Rehydration
20–110°C	15.7	64 percent
110–190°C	13.3	None
190°C—red heat	7.5	None
1075°C	(mullite formed)	—

ORIGIN OF HIGH-ALUMINA ALLOPHANE

Occurrence at cores of plagioclase crystals indicates a secondary origin of the high-alumina allophane, and probably it is a product of weathering rather than deuteric alteration, for such effects as chloritization of biotite, sericitization of K-feldspar, and saussuritization of plagioclase are completely absent from the rock in which the allophane occurs. Several previous workers have noted formation of optically isotropic material in plagioclase at early stages of rock weathering (Grant, 1963, 1964; Bates, 1962), and, so far as Sierran rocks are concerned, Bateman *et al.* (1963, p. 15), in speaking of plagioclase, observe: "under certain conditions the cores have weathered out." That calcic plagioclase should be the first mineral to break down under surficial conditions fits well with the order of stability of minerals of igneous rocks towards weathering as established by Goldich (1938).

Alteration of plagioclase is the only indication of weathering in thin section of the allophane-bearing rock: mafic minerals appear perfectly fresh. There was, however, slight iron staining on the outcrop surface.

Considering the original composition ($\sim$An$_{40}$) of the cores of the

plagioclase grains, weathering of them to form allophane has resulted in considerable depletion in lime, soda and silica, and introduction of water. The situation is illustrated in Table 3, wherein a calculated analysis of plagioclase of composition An_{40} (column 2) is set out for comparison with the analysis of anhydrous high-alumina allophane recalculated to 100 percent (column 3). Of the several oxides involved, alumina has probably remained most constant, and the analysis of the fully-hydrated mineral (Table 1) has been recalculated (column 4) assuming constant Al_2O_3.

The specific gravity of An_{40} plagioclase is 2.67 g/cc but that of the allophane is 2.1 g/cc .No volume increase has taken place during alteration of plagioclase to allophane, however, because no evidence of expansion of plagioclase grains—such as offset of twin lamellae, cracks in host

TABLE 3. CHEMICAL CHANGES INVOLVED IN WEATHERING OF PLAGIOCLASE
TO FORM HIGH-ALUMINA ALLOPHANE

Oxide	An_{40} Plagioclase	Anhydrous allophane	Fully hydrated allophane, Al_2O_3 constant
SiO_2	58.1	23.8	8.4
Al_2O_3	26.6	75.2	26.6
CaO	8.4	0.46	0.16
Na_2O	6.9	0.38	0.13
K_2O	trace?	0.22	0.08
H_2O	—	—	20.4

minerals radiating from enclosed weathered plagioclase—has been seen. (Fig. 1). Assuming Al_2O_3 to have remained constant during reaction, calculation of the actual amounts of material involved shows, on the contrary, that appreciable volume loss has been produced by alteration of plagioclase to allophane. There is, however, no textural evidence of contraction, and the loss is assumed made up for by creation of minute pore spaces in the mineral or possibly introduction of water in excess of the amount adsorbed by the mineral.

Previous workers have suggested origins of amorphous alumina-silica weathering products. For example, Bates (1962) studied plagioclase weathering in Hawaiian andesites and found that halloysite forms first, by alteration of the core and then the rim of the plagioclase, and gibbsite is subsequently produced by desilication of halloysite. He observes (p. 315) than an " . . . amorphous transition state, probably ranging in composition from allophane to Al-gel exists as part of the change from halloysite to gibbsite." This range of composition includes the high-alumina allophane but as far as the present occurrence is concerned there

is no evidence for such a transition state, because there is no evidence of halloysite or gibbsite. Tamura and Jackson (1953) have suggested a mechanism for allophane formation. The sequence involves (1) formation of crystalline gibbsite from amorphous $Al(OH)_3$; (2) dehydroxylization of gibbsite; and (3) addition of silica in solution, the oxygens in silicon-oxygen tetrahedra substituting for lost hydroxyls, and silica and alumina then linking to form a random structure—allophane. But this mechanism requires dehydration and silication, whereas formation of the allophane has involved considerable hydration together with desilication. The present author would tentatively suggest the high-alumina allophane may have developed as an initial amorphous weathering product of plagioclase without any intervening stages. Alteration most probably began when water, introduced along fractures and cleavage traces, produced hydrolysis and dissolution; weathering solutions may well have been slightly acid owing to dissolved CO_2, but andesine is slightly alkaline upon hydrolysis (Stevens and Carron, 1938) and the situation could have been modified accordingly. Desilication of the feldspar must, however, have taken place within a pH range of 5 to 9, an interval within which alumina is relatively insoluble and silica is soluble in low concentration (Keller, 1964). The writer is not prepared to suggest why high-alumina allophane has formed instead of more normal products such as halloysite or common allophane, but it is emphasized that conditions for development of the aluminous mineral were not unusual or extreme. The allophane-bearing sample was collected from the top of an outcrop of granodiorite in a very well drained situation; no soil had developed and no vegetation was present. The occurrence is sufficiently commonplace as to raise the question why high-alumina allophane has not been recognized more often as a weathering product of plagioclase.

ACKNOWLEDGMENTS

REFERENCES

AGRELL, S. O. AND J. V. SMITH (1960) Cell dimensions, solid solutions, polymorphism and identification of mullite and sillimanite. *J. Amer. Ceram. Soc.* **43**, 69–76.

BATEMAN, P. C., L. D. CLARK, N. K. HUBER, J. G. MOORE AND C. D. RINEHART (1963)

The Sierra Nevada batholith—a synthesis of recent work across the central part. *U. S. Geol. Surv. Prof. Pap.* **414-D,**

BATES, T. F. (1962) Halloysite and gibbsite formation in Hawaii. *Clays Clay Minerals, Proc. Nat. Conf. Clays Clay Minerals* [1960] **9,** 315–328.

BIRREL, K. S. AND M. FIELDES (1952) Allophane in volcanic ash soils. *J. Soil Sci.* **3,** 156–166.

BROWN, G. (1955) Report of the clay minerals group subcommittee on nomenclature of the clay minerals. *Clay Minerals Bull.* **2,** 294–302.

DANA, J. D. (1885) *A System of Mineralogy. Descriptive Mineralogy.* 5th ed. John Wiley and Sons, New York.

DES CLOISEAUX, A. (1862) *Manuel de Minéralogie,* **1,** 200. E. Thunot and Co., Paris.

DOELTER, C. (1917) *Handbuch der Mineralchemie, v.* 2, *part* 2, p. 37. Theodor Steinkopf, Dresden and Leipzig.

EVANS, H. T., D. E. APPLEMAN AND D. S. HANDWERKER (1963) The least-squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method (abs.). *Amer. Crystallogr. Ass. Ann. Meet., Program,* p. 42–43.

GOLDICH, S. S. (1938) A study in rock weathering. *J. Geol.* **46,** 17–58.

GRANT, W. H. (1963) Weathering of Stone Mountain granite. *Clays Clay Minerals, Proc. Nat. Conf. Clays Clay Minerals* [1962] **11,** 65–73.

——— (1964) Chemical weathering of biotite-plagioclase gneiss. *Clays Clay Minerals, Proc. Nat. Conf. Clays Clay Minerals* [1963] **12,** 455–463.

HEY, M. H. (1955) *An Index of Mineral Species and Varieties Arranged Chemically.* British Museum, London.

KELLER, W. D. (1964) The origin of high-alumina clay minerals—a review. *Clays Clay Minerals, Proc. Nat. Conf. Clays Clay Minerals* [1963] **12,** 129–151.

KERR, P. F. AND P. K. HAMILTON (1949) Glossary of Clay Mineral Nanes. *Amer. Petrol. Inst., Proj.* **49,** *Prelim. Rep.* **1.**

MITCHELL, B. D. AND V. C. FARMER (1962) Amorphous clay minerals in some Scottish soil profiles. *Clay Minerals Bull.* **5,** 128–144.

ROSS, C. S. AND P. F. KERR (1934) Halloysite and allophane. *U. S. Geol. Surv. Prof. Pap.* **185-G,** 135–148.

ROST, R. (1944) Contribution to the knowledge of clay minerals. *Rozpr. Ceske Akad. Ved.* **54,** 1–28.

SEARLE, A. B. AND R. W. GRIMSHAW (1959) *The Chemistry and Physics of Clays and Other Ceramic Materials.* Interscience Publishers Inc., New York.

SNETSINGER, K. G. (1965) *Petrology and mineralogy of metamorphic and intrusive rocks, northwest part of the Bass Lake quadrangle, Madera and Mariposa Counties, California.* Ph.D. Thesis, Stanford University.

STEVENS, R. E. AND M. K. CARRON (1948) Simple field test for distinguishing minerals by abrasion pH. *Amer. Mineral.* **33,** 31–49.

TAMURA, T. AND M. L. JACKSON (1953) Structural and energy relationships in the formation of iron and aluminum oxides, hydroxides, and silicates. *Science* **117,** 381–383.