HYDROTHERMAL KAOLINIZATION (ENDELLITIZA-TION) OF VOLCANIC GLASSY ROCK

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ABSTRACT

A vitreous, perlitic rock near Etzatlán, west of Guadalajara, Mexico, has been argillized by hot spring activity. A continuous outcrop from fresh rock to relatively pure clay (halloysite) is exposed, and samples were collected along it to trace the progressive alteration. Alkali metals and silica were leached during argillation, as was shown by analyses of the solid samples and solutions from laboratory hydrolysis of the rock. The interpretation that the original clay mineral was endellite is supported by experiments treating the clay with K-acetate and ethylene glycol. The random arrangement of Si-O-Al in the glass is thought to have favored development of disordered stacking in the clay mineral formed, hence endellite, and random distribution of very fine-grained clay crystals in the mass of clay.

INTRODUCTION

Kaolinization of both aphanitic and phaneritic (especially the granite clan) igneous rocks is relatively well documented, but few occurrences of commercial-size deposits of kaolin minerals that developed from glassy rocks have been reported. The purpose of this paper is to record and briefly describe the progressive kaolinization, by hydrothermal action, of a glassy rock equivalent in chemical composition to granite, which occurs west of Guadalajara, in the state of Jalisco, Mexico. The clay mineral present is halloysite (approximately $2H_2O$) as identified by X-ray diffraction and chemical analysis, but evidence will be offered subsequently which leads me to believe the original mineral was endellite (the $4H_2O$ member of the kaolin group); therefore the extant clay will be referred to as halloysite but its process of formation prior to dehydration as endellitization.

The clay deposit, which was abandoned commercially after several carloads of halloysite had been produced, is designated as the Etzatlán deposit because it is located about 10 km west and north of Etzatlán which, in turn is about 125 km west of Guadalajara. A more accurate land description, or location, of the mine was not available. The deposit was controlled at the time of my visit in 1957 by Sr. Servín. Travel to the mine for the last few kilometers was

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on horseback, although a dirt road to it, severely eroded by rain wash, had previously been passable to high-clearance trucks.

The clay occurs in a steeply dissected, hilly region having a local relief of about 100-150 m. The exposed rocks in the immediate region are Tertiary volcanics, mainly flows that are commonly brecciated and partially and irregularly pumiceous, and range in texture from clouded light gray glass to porphyritic aphanites (probably rhyolites). This region is part of the eastwest volcanic axis of Mexico, characterized not only by erupted lava but also by notable hydrothermal activity. For example, present-day hydrothermal activity, presumably typical of that which produced the Etzatlán clay, includes the steam vents (drilled for power production tests) near Rayon in Hidalgo (State) north of Mexico City, and the Los Azufres hot spring region near Ciudad Hidalgo in the state of Michoacan. Clay was mined in 1957 near Rayon, and at Los Azufres both clay minerals and clay-size cristobalite were deposited at the orifices of the hot springs. Most of the commercially produced refractory clay (kaolin group and alunitic kaolin group) in Mexico has originated by hydrothermal alteration of porphyritic aphanites, tuffs, and metamorphic silicate rocks, or by replacement of limestone by hydrothermally transported materials.

DESCRIPTION OF THE DEPOSIT

The Etzatlán clay deposit provides an opportunity to trace for 50 ft the transitional argillation of the relatively fresh glassy country rock to altered material that is almost completely halloysite. The core of the deposit is located in a hillside spur which deflects a meander in a small stream. A continuous rock section grading from fresh rock to clay is exposed in the side of a roadway which has been dug along the stream bank to the clay. Samples for study were collected along the road and from the rooms in the clay mine.

The exposed part of the deposit is roughly elliptical in plan, having a major axis about 35-40 ft in length over which pronounced argillation has occurred; but only an inner core of this deposit, perhaps not more than 5-20 ft in diameter and now mostly depleted, was transformed into sufficiently pure halloysite to be merchantable. Alteration diminishing in intensity was continued peripherally outward perhaps as much as 50 ft beyond the 35-to 40-ft dimension assigned to the clay deposit, per se.

A thickness, or height, of about 25 ft of clay is exposed, but probably the clay extends over a distance at least 25 ft more if boundaries on the vertical axis do not converge more rapidly than do those laterally. Since the alteration is undoubtedly hydrothermal, at least some clay may extend for some distance downward, but not indefinitely—as might be desired by prospectors and producers of clay. Observation and experience with other extensively opened and mined clay deposits of hydrothermal origin in Mexico show that the depth to which such clay deposits extend is limited by the following geologic factors.

The extent of the clay obviously is limited to the thickness (and lateral distribution) of a parent rock of favorable composition. Nevertheless, within a large body of rock that is potentially productive of clay, the upper zone that is near the earth's surface, say within 50–100 ft as an order of magnitude, is more likely to be extensively argillized than is the rock at greater depth for two reasons, despite the fact that the thermal energy derives from depth. First, the close access of hydrothermal solutions to country rock is enormously expanded very near the surface of the earth because of the highly increased multiplicity of rock jointing near the surface. Thus, hydrothermal solutions rising through only one, or few, large fissures from depth are divided profusely near surface into a vertical dendritic pattern analogous to the way the main trunk of a stream is divided horizontally into distributaries spread over an alluvial fan or delta. Second, although the thermal energy derives at depth, the major source of the water, warmed near the earth's surface, is meteoric water (shown by studies in Yellowstone National Park and elsewhere) which is obviously most abundant near the earth's surface. Moreover, the argillation of silicate igneous rock is essentially a hydrolysis reaction in which relatively fresh water (i.e. water not charged with products of rock hydrolysis) is most aggressive, and near-surface meteoric water is of this type. Therefore, under geological conditions where relatively small amounts of hydrothermal fluids are involved in argillation, as is the case in post-Early Tertiary, extrusively or volcanically induced clay alteration in Mexico, the most extensive (volumetrically) argillation of rock by hydrothermal action is shallow and near surface. However, on the other hand, where relatively copious volumes of hydrothermal fluids are involved and alteration is induced by plutonic or intrusive action, as reported in the Cornwall region of England, very extensive argillation can and does develop at great depth.

The Etzatlan clay is relatively homogeneous in structure, being free from many joints or slickensides. Apparently there was little bulk volume change during the argillation process. The volume of the constituents removed by dissolution was compensated for by (1) addition of combined water during argillation, or (2) increased porosity and decreased density of the clay, or (3) complete breakdown of the rock and sedimentation in the hot water within the most active parts of hot spring channels. Similarly, in other Mexican hydrothermal kaolin-group deposits the writer has noted minimal volume change and slipping in those developed from argillized silicate rocks, but notably more slickensiding and volume adjustment in kaolin replacements of carbonate rocks.

MATERIALS STUDIED

Clay and rock samples were collected from the center (purest clay) of the deposit, and outward through less altered rock, at intervals of 15-25 ft, along the roadway excavated to the clay, as follows.

Et no. 1. Off-white to very light tan clay from the center of the deposit. This is the best, purest, softest, and most plastic clay.

Et no. 2. Outside (10 ft) portal of mine, 25 ft outward from no. 1. Similar to, but slightly harsher than, no. 1.

Et no. 3. On roadway, 40 ft outward from no. 1. Gritty, harsh, earthy rock, light tan.

Et. no. 4. In road cut, 70 ft from no. 1. Tan, gray, slightly argillized, crumbly rock fragments.

Et no. 5. In road cut, 90 ft from no. 1. Powdery rock fragments, slightly argillized, gray to light tan.

Et no. 6. Fresh, light to dark gray, vitreous rock, about 100 ft from no. 1. Brecciated glass, slightly perlitic, containing occasional pumiceous, gravel-sized fragments; extensively and irregularly cracked, probably as a result of tension during solidification, producing sharp-edged, angular corners and edges along non-intersecting cracks; therefore the rock does not crumble.

LABORATORY STUDY AND ANALYTICAL RESULTS

Thin sections of the samples were examined for variations in texture and mineralogy. Complete chemical analyses of samples 1, 3, 4, and 6 are presented in Table I. X-ray diffractograms were run on the solid materials including processing with K-acetate and ethylene glycol by an extended modification of Wada's (1961) technique. The clay obviously represents the relatively insoluble products of the hydrolysis of the parent rock from which the relatively soluble products have been dissolved. To study these soluble products, fresh and partly altered rock was pulverized under water in the laboratory and the liquid was analyzed for dissolved ions as follows.

A 10-g portion of each sample, after being crushed to about minus 8-mesh particles, was ground for 1 hr in 100 ml of double-distilled (Na free) water in a mechanically driven fused alumina mortar and pestle grinder. This procedure, i.e. amount of rock, water, time of grinding, etc., was adopted after considerable experimentation to yield maximum information on rock and mineral hydrolysis from a feasible, single-grind laboratory process. Details of the experimentation and procedure are prepared for publication elsewhere in a report on hydrolysis and weathering of silicate rocks, but the essential steps taken are outlined here.

The pH of the slurry was measured in the mortar at the end of the grinding period, and the suspension was then centrifuged for 6 hr (or 8 hr, if necessary) in 100-ml polyethylene tubes at 1900 rpm in an International size 2 centrifuge to separate clear liquid from the pulverized particles. The clear liquid was poured into polyethylene containers, diluted 1:1 with double distilled water, and analyzed for the common rock-forming elements. Dissolved silica was determined by colorimetry, dissolved Al by fluorimetry, dissolved Na and K by flame photometry, and dissolved Ca and Mg by emission spectroscopy using spark excitation from porous cup electrodes. Precision of these results is about plus or minus 10 percent of the amounts reported where they are greater than 1-2 ppm but under 1 ppm, variation may be 50–100 percent of that reported. Measurements of pH of the pulverized slurry are good to about 0.1 pH unit. Analyses of the solutions and solid products are reported in

	Ā	5	E	4	Ē	-3	Et	-1
	Percent by weight	Cation ratio by number	Percent by weight	Cation ratio by number	Percent by weight	Cation ratio by number	Percent by weight	Cation ratio by number
Ignition loss (H_2O) SiO ₂ SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ Fe ₂ O ₃ MgO K ₂ O Na ₂ O Na ₂ O SO ₃ MnO ₂ TiO ₂	$\begin{array}{c} 4.41\\ 7.137\\ 7.137\\ 16.04\\ 0.70\\ 0.70\\ 0.12\\ 0.12\\ 0.12\\ 2.66\\ 0.03\\ 0.01\\ 0.01\end{array}$	$\begin{array}{c} 0.489\\ 1.190\\ 0.314\\ 0.008\\ 0.008\\ 0.002\\ 0.095\\ 0.095\\ \end{array}$	6.26 6.26 6.36 1.14 1.14 0.04 0.16 0.12 2.40 0.03 0.03 0.01 0.01	0.694 1.135 0.354 0.014 0.003 0.075 0.078 0.078	$\begin{array}{c} 14.72\\ 48.64\\ 33.25\\ 1.96\\ 0.07\\ 0.12\\ 0.42\\ 0.34\\ 0.28\\ 0.28\\ 0.28\\ 0.28\\ 0.12\\ 0.01\\ 0.01\end{array}$	$\begin{array}{c} 1.640\\ 0.810\\ 0.652\\ 0.025\\ 0.001\\ 0.001\\ 0.002\\ 0.002\\ 0.001\\ 0.001\\ 0.001\\ 0.001\\ 0.001\\ 0.001\\ \end{array}$	$\begin{array}{c} 14.64\\ 47.45\\ 34.65\\ 3.15\\ 0.08\\ 0.12\\ 0.25\\ 0.25\\ 0.24\\ 0.02\\ 0.02\\ 0.01\\ 0.01\\ \end{array}$	1.624 0.791 0.680 0.027 0.002 0.002 0.005 0.005 0.005
Total	99.95		99,96		99.96		99.95	
	Cation rati Et-6 H ₃ Et-4 H ₃ Et-3 H ₅ Et-1 H ₄	ios, or "formul 11 K _{0.605} N ^E 192 K _{0.434} Na 193 K _{0.021} N ^E 17 K _{0.015} N ^E	as,'' arbitraril a.54 Ca.013 0.441 Ca.017 0.028 Ca.006 a.021 Ca.006	y holding Al a Mg.013 Fe'' Mg.011 Fe'' Mg.031 Fe'' Mg.034 Fe''	t 2.00, as Al ₂ 0.000 Fe ^(*,0.05) 0.000 Fe ^(*,0.07) 0.000 Fe ^(*,0.07) 0.003 Fe ^(*,0.07)	00 I Al _{2.00} Si _{7.5} , Al _{2.00} Si _{3.9} , Al _{2.00} Si _{2.4} Al _{2.00} Si _{2.4}	p- 01 00 00	
Et-6, fresh rock, abc Et-4, argillized, crun Et-3, gritty, harsh, ε Et-1, clay from cent	nut 100 ft from nbly rock, 70 j sarthy, clay-ro er of deposit.	ı Et-l. ft from Et-l. ick, 40 ft from	Et-1.					

TABLE 1.—CHEMICAL ANALYSES AND CATION RATIOS

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Analyses by Bruce Williams Laboratories, Joplin, Missouri.

https://doi.org/10.1346/CCMN.1961.0100129 Published online by Cambridge University Press

Tables 2 and 1, respectively, which will be discussed after an examination of X-ray diffractograms of the solids.

In Fig. 1 are shown X-ray diffractograms of fresh perlitic rock, no. 6 (obviously not detectably crystalline); partially argillized rock, no. 4; and halloysite (with a small amount of quartz impurity), no. 1. These diffractograms are typical and need no further comment for the sequence. Following



FIGURE 1.—X-ray diffractograms of fresh perlitic rock, no. 6; partly argillized rock, no. 4; and halloysite, no. 1; from the Etzatlán deposit. Ni-filtered copper radiation.

these runs the clay from no. 1 was ground dry with K-acetate for 25 min (Wada, 1961) and allowed to set overnight, whereupon its 001 spacing had been entirely expanded to 14 Å. This clay was then washed 4 times with distilled water to remove the K-acetate, and finally washed with an aqueous solution of ethylene glycol. The 001 spacing was thereby reduced to a broad 10 Å peak tailing toward 12 Å. The same sequence of results was obtained by similar processing of Indiana endellite which yielded a 10 Å spacing in its original wet condition and a 7 Å spacing when dehydrated. I interpret from these observations that the original Etzatlán clay was endellite which has

	Et-	6S	Et-	58	Et	-4S	Et-	3S	Et	IS
	udd	Μη	bhm	μμ	bpm	мη	mqq	мη	uudd	μи
Si	6.3	0.224	8.02	0.286	6.08	0.217	7.06	0.247	4.14	0.145
Al	0.216	0.008	0.06	0.002	0.094	0.035	0.40	0.015	0.032	0.012
Ca	1.94	0.049	1	I		1	1	1]	I
M_g	0.38	0.016	1	1	0.18	0.008	0.14	0.006	0.018	0.001
Я	3.0	0.078	5.6	0.144	8.2	0.21	13.4	0.344	11.2	0.287
Na	9.0	0.391	11.6	0.505	5.6	0.243	6.0	0.26	4.6	0.20
Total	20.836		25.28		20.154		27.00		19.99	
$^{\mathrm{pH}}$	8.8		7.5		7.6		7.3		6.6	
Et-6S	Gram mols in ro Gram micromols Soln./rock	ck in solution	K _{0.605} N80. K _{0.214} Na _{1.} 0.36 2.	54 Ca _{0.013} 32 Ca _{0.165} 4 12.7	Mg0.013 & Mg0.013 A Mg0.054 A	M2.00 Si7.57 J0.027 Si7.57 0.014				

TABLE 2.--DISSOLVED HYDROLYSIS PRODUCTS

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been dehydrated, but not quite completely (analysis Et-3 in Table 1), to halloysite $(2H_2O)$. The behavior of several kaolin-type minerals on K-acetate treatment is discussed in greater detail in a report by Miller and Keller (this Volume). Nevertheless, regardless of whether the glassy rock was altered to endellite or halloysite $(2H_2O)$, the following chemical considerations are pertinent.

In Table 1 are shown the chemical compositions of samples 1, 3, 4, and 6 expressed conventionally in weight percent, and also with these oxide-weight ratios converted to numbers of cations represented by the oxide, such as H from H_2O lost (ignition loss), Si from SiO₂, Al from Al₂O₃, etc. The cation ratios have been further recalculated by arbitrarily holding Al constant at 2.00 (as in kaolinite, $H_4Al_2Si_2O_9$), as is shown in the lower part of the table, which provides a basis for comparing the analyses and tracing the sequence of chemical changes during alteration.

The fresh parent rock, Et-6, has a chemical composition typical of perlite and midway between obsidian and pitchstone, as is observed from the relatively high content of combined water (4.41 percent). At the other end of the table, the purest clay sample, Et-1, is close to theoretical hallovsite-2H₂O in composition, but differs from it in being about 1.25 percent high in SiO_2 , 4.8 percent low in Al₂O₃ but containing 2.15 percent Fe₂O₃ impurity, and 0.6 percent high in H₂O. Samples Et-4 and Et-3 have compositions that show progressive alteration from Et-6 to Et-1, when Al is arbitrarily held constant, a condition that does not completely prevail but is closely approximated, as will be shown in the analysis of hydrolytic solutions. By comparing the cation ratios in the samples from Et-6 to Et-1 it is seen that SiO, is progressively lost as argillation proceeds, and that the rate of desilication is most rapid when the difference in composition of the parent rock differs most from that of the product. Iron oxide is slightly concentrated during alteration. The alkali metal ions, K and Na, are lost at the highest rate between Et-4 and Et-3, that is, in a state of partial alteration. Water (actually H) is added in combination as alkali cations are removed. The higher water content of Et-3 over Et-4 may possibly be due to strong hydration of perlitic glass accompanying the hydration during argillation, or more probably to intermediate hydration, i.e. incomplete dehydration, of clay between halloysite and endellite.

The dissolved products of hydrolysis of samples Et-6, 5, 4, 3, and 1 are recorded in Table 2 as parts per million (by weight) and recalculated as micromoles. The pH of each slurry, which was measured by inserting the glass electrode into the powdered residue (thereby measuring the abrasion pH of the rock and the clay, Stevens and Carron, 1948), is also shown. The pH declines from 8.8 for the alkali-rich rock to 6.6 for the impure halloysite, except for slight reversal in trend between Et-5 and Et-4, which may be anomalous. The pH values observed parallel those which have been reported for feldspars, abrasion pH 8 to 9, and kaolinite, abrasion pH 6 to 7.

Under the laboratory conditions in which the fresh rock was pulverized under water and hydrolyzed, approximately 21 ppm by weight of the rock-

forming cations was dissolved; the solution is designated Et-6S. The ratio in solution of alkali metals to Si is 2.1 to 1, not far from Na₂SiO₃, which may, or may not, have significance. The ratio of gram micromoles in solution to gram moles in the rock for Et-6S, after recalculating the dissolved constituents so that the subscript for Si is 7.57 in both analyses, is shown below the pH values. Only a slight amount of Al is dissolved (a fact long known to geologists) giving basis for holding Al to 2.00 in the calculations in Table 1. The presence of Al in solution also decreases the solubility of silica (Okamoto, Okura and Goto, 1957). Na is dissolved in higher ratio to its occurrence in rock than is K. Ca is more susceptible than Mg to solution in hydrolysis, although the amounts of each available are so small that the actual numbers have probably little significance beyond an order of magnitude. The fact that the scantily occurring elements, here the alkaline earth elements, showed higher relative enrichment in solution than the more abundant ones, alkali earths, is in accord with similar behavior observed in hydrolyzing individual minerals (Keller, Balgord and Reesman, in press, J. Sediment Petrol).

Comparison of the amounts of cations dissolved in the sequence Et-6S to Et-1S shows approximately 7 ppm silicon from the altering rock samples, and 4 ppm from the halloysite. Apparently the 7 ppm represents a condition approximating stability in this particular hydrolysis experiment. Ca and Mg are removed during early stages of rock alteration. The Na dissolved during hydrolysis declines as rock alteration proceeds towards hallovsite. K dissolved from rock hydrolysis increases with advance in halloysitization, an observation that was unexpected; neither was a high dissolved load expected from pulverized halloysite. Four interpretive, possible explanations may be offered for these observations. Alkali metal ions, especially K, may be sorbed by the clay as it develops from the rock, and these ions may be released by dialysis (the Donnan effect) as the clay is pulverized in distilled water. Secondly, hydrothermal waters rising through rock that is undergoing hydrolysis may become saturated with dissolved hydrolysis products and, upon soaking en route through the clay in the deposit above, load all cation exchange sites on the clay particles with K and Na which are then readily released upon pulverizing in distilled water. Thirdly, many kaolin-group deposits of hydrothermal origin in Mexico contain some, to much, alunite, and it is possible that the components of alunite are present in this halloysite, Et-1, but too scanty to be detected by the ordinary techniques of mineral identification. Fourthly, the fact that KOAc can and does prop open the basal spacing of the kaolin minerals, as in Wada's treatment, leads one to speculate that mobile K ions in the solution in which endellite is precipitated and crystallized may be contributory, or even essential, to the genesis of endellite. One may speculate conversely that, if K is not mobile, but instead is fixed within an antecedent phyllosilicate, muscovite for example (Sand, 1956) then kaolinite, not endellite, is formed (Miller and Keller, this Volume). If the speculation about K being essential to the formation of endellite is valid, the increased amount of K in endellite may be real and significant.

MECHANISM OF ARGILLATION

A solid silicate, crystalline or glassy, may be converted to another solid, a phyllosilicate clay mineral, such as endellite, presumably by several mechanisms: solid to solid, by crystal surface rearrangement (DeVore, 1959); feldspar to mica to kaolinite (Sand, 1956); solid by way of an intermediate liquid phase to solid (Garrels and Howard, 1959); and under the influence of inherited energy and previous crystal structure, or "memory" of a prior structure (Sand, 1956; Keller, 1957). Besides the alteration sequence of feldspar to mica to kaolinite (Sand, 1956; Garrels and Howard, 1959; Meyer and Hemley, 1959), feldspar may be weathered directly to endellite (Sand, 1956; Ponder and Keller, 1960). Direct endellitization of feldspar was described by Sand (1956, p. 38) for Appalachian occurrences, as follows:

Effective leaching from the feldspar of all its bases probably destroys its structure and the colloidal silica and alumina are arranged into the random structure of hydrated halloysite. It is significant that hydrated halloysite, not its dehydrated product, always was present except where samples were obtained from dried exposures.

Direct endellitization of the Etzatlan glass without intermediary mica formation is indicated by direct invasion of the glass by very fine-grained, low-birefringent clay without even any suggestion of mica between the clay and the glass. Curiously, the argillation of the perlite began, not as a continuous wave spreading inward from microscopic eracks within the rock, in the manner that ordinary surface oxidation or massive hydrothermal alteration spreads from a joint pattern in rocks, but instead alteration began in the interior of "pearls" in the perlitic structure (Plate 1). A similar mechanism of argillation, attributed to outward diffusion of metal cations, was reported by Bates (1962, pp. 322, 323) in the alteration of basalt in Hawaii. On a macroscopic scale, however, the zone of internally altered pearls advanced from completely altered material into the fresh rock.

The clay both in the forefront of alteration and back in the completely argillized portion is exceedingly fine-grained and randomly oriented, as is indicated by extremely weak interference colors and no organized pattern of preferred orientation of interference color (crystal orientation). This random distribution of the tiny clay crystals (crystalline to X-ray) is interpreted as being influenced by the random organization of Si–O–Al-metal ions in the parent glass, and by the probability that the Si–O–Al structure remaining after the leaching of the metal cations would leave behind a poorly organized residue that would be a likely progenitor for poorly organized endellite. The hydrothermal leaching was sufficiently efficient, and perhaps at a low enough pH, that a member of the kaolin group (not a 2:1 layer group) of clays was formed. It would be interesting in light of Sand's observation of the origin of kaolinite to know if any volcanic glasses have altered to kaolinite rather than to endellite.



PLATE 1.—Photomicrographs showing argillation (clouded, darkened areas) at interior of perlitic structure, Et-4. On eyepiece micrometer 10 small divisions represent 0.2 mm on specimen.

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ACKNOWLEDGMENTS

The chemical analyses of the rock samples were financed under a grant from the University of Missouri Research Council, and the analyses of hydrolytic solutions were made by Mr. Arthur Reesman under the auspices of National Science Foundation Grant 9159.

REFERENCES

- Bates, T. F. (1962) Halloysite and gibbsite formation in Hawaii: in *Clays and Clay Minerals*, v. 9, Pergamon Press, New York, pp. 315-328.
- DeVore, G. W. (1959) The surface chemistry of feldspars as an influence on their decomposition products: in *Clays and Clay Minerals*, v. 6, Pergamon Press, New York, pp. 26-41.
- Garrels, R. M., and Howard, Peter (1959) Reactions of feldspar and mica with water at low temperature and pressure: in *Clays and Clay Minerals*, v. 6, Pergamon Press, New York, pp. 68-88.
- Keller, W. D. (1957) The Principles of Chemical Weathering: Lucas Bros., Columbia, Missouri, 111 pp.
- Meyer, Charles, and Hemley, Julian (1959) Hydrothermal alteration in some granodiorites: in *Clays and Clay Minerals*, v. 6, Pergamon Press, New York, pp. 89–100.
- Miller, W. D., and Keller, W. D. (this volume) Differentiation between endellitehalloysite and kaolinite by treatment with potassium acetate and ethylene glycol: in *Clays and Clay Minerals*, Pergamon Press, New York.
- Okamoto, Go, Okura, Takeshi and Goto, Katsumi (1957) Properties of silica in water: Geochim. et Cosmochim. Acta, v. 12, pp. 123-132.
- Ponder, Herman, and Keller, W. D. (1960) Geology, mineralogy, and genesis of selected fireclays from Latah County, Idaho: in *Clays and Clay Minerals*, v. 8, Pergamon Press, New York, pp. 44-62.
- Sand, L. B. (1956) On the genesis of residual kaolins: Amer. Min., v. 41, pp. 28-40.
- Stevens, R. E., and Carron, M. K. (1948) Simple field test for distinguishing minerals by abrasion pH: Amer. Min., v. 33, pp. 31-49.
- Wada, Koji (1961) Lattice expansion of kaolin minerals by treatment with potassium acetate: Amer. Min., v. 46, pp. 78-91.