

GENESIS OF REFRACTORY CLAY NEAR GUANAJUATO, MEXICO

by

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ABSTRACT

Refractory clay, derived from hornblende chlorite schist that was hydrothermally altered along nearly vertical fractures and faults, occurs near Guanajuato, Mexico, a few kilometers south and east of the famous monument, El Cristo Rey. Part of the chlorite is expanding, i.e. probably mixed-layer vermiculitic chlorite or biotite. The most refractory clay is comprised chiefly of kaolinite, with variable amounts of finely crystalline quartz. Huge, thick "gossans" of silica have been deposited as surface-covers over the fractures; such silica gossans are fairly common over Mexican hydrothermal clay deposits and may be used as probable field guides to argillation.

The trend of mineralogical and chemical changes (analyses tabulated in the paper) during argillation of the Guanajuato material is traced in overlapping sequence, as follows:

(a) bleaching of green ferro-ferric silicates accompanied by oxidation of part of the iron to "limonite".

(b) leaching of alkali and alkaline earths accompanied by,

(c) partial desilication of parent silicate minerals yielding kaolinite whose flakes are commonly oriented parallel with the chlorite of the schist, mobile silica, and finely divided quartz intermixed with the kaolinite,

(d) refinement ("purification") of the clay by further kaolinization and removal of silica minerals and some iron oxide.

The final clay may run higher in silica than does its parent rock.

INTRODUCTION

REFRACTORY clay of hydrothermal origin occurs in a large district (about 20 km²) located 3 to 5 km north of the railroad siding Noche Buena, 7 to 10 km west of Guanajuato, Gto., Mexico. Early mining which began, more than 50 years ago, with small excavations directed toward easily accessible and selective extraction, was relatively unproductive of geologic information. During the last 10 years, systematic programs of mining and mapping have yielded a clearer picture of the geometric and geologic relationships of the clay to the country rock, (Hanson, 1965). The argillation process, as it operated in a representative deposit located in claim No. 140547 of Refractarios A. P. Green, S. A., Mexico City, will be discussed in this report.

GENERAL GEOLOGY OF THE DISTRICT

The main country rock of the district, and parent rock of the refractory clay, is a medium-grained green schist, striking generally N.-S. and dipping steeply to the west. Mineral(s) of the chlorite family dominate most of the schist, but pale green hornblende is prominent in many zones. The schist was thought by Edwards (1955) to have been derived from Mesozoic marine shales, possibly Triassic in age because they resemble lithologically those of Triassic age in Zacatecas to the north. According to Edwards the shales were metamorphosed during Laramide orogeny, when also diorite, granite, and other intrusives were emplaced beneath. Uplift, faulting, erosion, and volcanism followed. The red Guanajuato conglomerate of Eocene to Oligocene ages accumulated to more than 1000 m thickness in nearby areas, followed by deposition of rhyolitic pyroclastics and later andesitic and basaltic flows. High-angle faulting began, presumably in Miocene time, and continued in diminishing scale to the present.

The refractory clay has been developed along nearly vertical fracture zones in the schist by the action of rising water on the schist. Two lines of evidence show that argillation took place within the present geomorphic cycle. Large deposits of silica, in effect silica gossans, persist as surface caps over the tops of the clay veins, testifying that the present land surface served as a base for their deposition. Secondly, clay deposits tend to widen upward as would occur when rising waters diverged into jointing more profuse nearest the surface (present erosional surface) than at depth. Hot spring activity observed elsewhere along the volcanic axis in Mexico demonstrates similar flaring distributive venting near the present surface. Silica gossans are a common, but not necessary, accompaniment of hydrothermal clay deposits in Mexico. They may cap hydrothermal veins in volcanic rocks and shales, as well as in metamorphic rocks; thus they may serve as a tentative field clue to argillation.

The refractory clay, consisting mainly of disordered kaolinite and very fine grained quartz, is generally present adjacent to the fracture zone. As merchantable clay (at least PCE 30), it grades outward 1 to 40 m wide into the country rock, and thence through 2 to 20 m of diminishing bleaching and softening to imperceptible alteration of country rock. Thus, whereas refractory clay is produced only from the center of the alteration zone, clay useful for structural products might be taken (not now economically) from its outer zones.

ARGILLATION OF THE SCHIST

Samples were collected sequentially from the fresh schist veinward to high quality refractory clay. Presumably the specimens were essentially stratigraphic counterparts and lithologic equivalents prior to argillation, but exact equivalence is uncertain where metamorphism accompanied by fracturing,

movement, and profound alteration, has taken place across the series. Material for thin sectioning, X-ray diffraction, and chemical analysis was taken from single hand specimens. A hornblende-containing series was studied in greatest detail.

Fresh Schist, No. 1

In thin section of the hornblende-rich rock, the hornblende ranges from about 10 to 30%. It occurs in sub-parallel ovoid sheaves of fine, pale needles, and also in thin wavy stringers, and as sparse needles penetrating feldspar metacrysts. A few pyroxene grains, perhaps 5% of the rock, yield to hornblende across ragged borders.

Chlorite which accompanies the hornblende grades outward from the sheaves of hornblende needles, and is mixed with but commonly dominates the stringers. Parts of the stringers may show high birefringence indicating hornblende and possibly a highly birefringent phyllosilicate, but other inter-laminations and alternating broader, wavy ribbons are dominantly chlorite. It has optical properties of prochlorite. Chlorite is estimated at approximately 30% of the hornblende-rich schist but will be higher, perhaps 60%, in hornblende-lean varieties.

Portions of schist in room-dry condition yield basal spacings from 14.3 to 14.9 Å; the base of the diffraction peak is broad and skewed slightly toward the smaller spacing side. Glycolation expands the spacing to 16.5 Å. Another schist sample, selected in the field as especially chloritic, yields a basal spacing of 13.9 Å when room dry, and 14.2 Å when glycolated. Heating a 14.6 Å-sample to 550° for 4 hours collapses it to 13.9 Å and reduces the area under the 14 Å peak from approximately 125 units to 10 units, but develops a broad peak that is highest at 9.0 Å and descends in a symmetrical saddle connecting with the 13.9 Å peak. From these responses, the phyllosilicate is tentatively identified as follows: the outcrop mineral is probably a vermiculitic alteration product (birefringence too high for pure chlorite) of chlorite that expands upon glycolation and collapses upon heating to mixed-layer mica-anhydride (?) and chlorite.

Feldspar, which is mostly fine-grained and untwinned but interspersed with a few larger crystals, occasionally twinned by Carlsbad or polysynthetic laws, comprises 25 to 40% of the microscope fields. Low relief (index) in thin section is consistent with either K-feldspar or, more probably, plagioclase up to andesine in Ca content.

Subhedral, tiny (same size as feldspar) grains of pale epidote, up to about 8% of the rock, are scattered variably midst the fine-grained feldspar. A small amount of iron oxide is present in scattered grains of hematite-bordered magnetite, and in reddish brown flakes separating schist folia.

Chemical analyses of the rocks, presented in Table 1, will be discussed in detail later.

TABLE 1.—CHEMICAL ANALYSES OF GUANAJUATO SPECIMENS

	1	2	3	4	5
SiO ₂	45.68	47.31	60.64	62.60	57.20
Al ₂ O ₃	17.26	16.43	23.77	23.68	28.54
Fe ₂ O ₃	9.10	14.46	2.01	0.99	0.31
FeO	1.81	0.71	0.39	0.21	0.26
MgO	7.10	2.32	0.32	0.09	0.04
CaO	6.68	7.09	1.94	1.25	1.25
K ₂ O	0.18	0.16	0.09	0.22	0.06
Na ₂ O	2.50	1.62	0.15	0.13	0.13
TiO ₂	1.07	2.02	1.71	1.54	1.54
MnO ₂	0.17	nil	nil	—	—
P ₂ O ₅	0.15	0.27	0.08	0.09	0.15
Loss ig	7.88	7.31	8.85	8.72	10.10
H ₂ O	0.37	0.25	0.01	0.41	0.37
Total	99.95	99.95	99.96	99.93	99.95

Analyses by Bruce Williams Laboratories, Joplin, Mo.

Altered Schist, No. 2

First-stage alteration of the schist, recognizable on the outcrop, shows slight dulling of luster and gradation from green to greenish-yellow color. The schist is friable, and breaks easily along both foliation planes and irregular transverse fractures which are lined usually by paper-thin, brownish iron-oxide films.

In thin section, plain light, most of the transparent color seen in the fresh rock is changed to an opalescent, very light yellowish brown. Opalescence originates probably from very tiny crystals (or voids?) commonly aggregated in small clouded flecks. The change toward uniformity in diaphaneity suggests that alteration is developing uniformity in rock composition, except that some schistose structure is still poorly preserved by sub-parallel orientation of discontinuous iron-oxide streaks and light-grey, intervening flecks. Vestiges of silicate minerals richest in iron have become diffuse dark brownish areas. Some transverse iron-oxide veining is observable. Sporadic thin lenses of very fine-grained quartz concentrations are aligned parallel to the schistosity.

Between crossed polars small, elongate, rather uniformly birefringent (orange to red of first order), ragged-edged shreds (length 2 to 5 times width) are oriented mainly in the direction of schistosity. Perhaps one-fifth, and elsewhere one-third, of the birefringent shreds are non-parallel to schistosity. Quartz is unchanged, and remnants of the larger feldspar crystals remain only slightly clouded and altered.

The thin section reveals that hydrothermal alteration begins with oxidation

of the iron, and a first-stage "digestion-homogenization" of the mafic silicate minerals.

The basal spacing of "chlorite" in No. 2 is: room dry, 14.2 Å; glycolated, 16.6 Å; and heated to 500° for 4 hr, a broad arch from 9.0 to 10.2 Å. Thus a probable mixed-layer, swelling (vermiculitic?) chlorite remains, which collapses upon heating to a mixed-layer mica complex (?). Quartz is weakly recorded.

Argillized Schist, No. 3

The outcrop and hand specimen at this stage of alteration shows very faint schistosity in some parts of the rock but none in others. The iron oxide mineral is reddish and, except where blended with chalky white clay spots, yields a mottled pinkish-white rock. Cross-cutting, very thin joints are clay-filled and white. The rock is still hard enough that it breaks irregularly, partly along remnant planes of schistosity, and partly cross-cutting along clay-filled fractures.

The thin section in plain light shows a slight parallelism of iron-oxide streaks and flecks. The section is less opaque than is No. 2; i.e. "homogenization" and coarsening of mineral crystals have resulted in less light scatter and reflection.

Between crossed polars, a mosaic of fine mineral particles having first-order birefringence shows very slight remnant trace of the "shreds" cited in No. 2. The low, first-order birefringence indicates increased "homogenization" toward a lower birefringent mineral (kaolinite) than is present in No. 2. Interference color in the larger crystals is too high for pure kaolinite, but that of the smaller crystals is compatible with the low birefringence of the kaolin group. Fine- to medium-grained quartz is developed in small veins and occasional isolated grains. Faint schistosity, delineated by the remnant shreds, persists.

An X-ray diffractogram shows a notably high, narrow, sharp peak at 7.1 Å, and another one well defined at 3.35 Å, the 001 and 002 of kaolinite, but a weak, unresolved band from 4.1 to 4.3 Å indicates a very low degree of regularity. Quartz is prominently recorded.

Harsh, "Rocky", Slightly Schistose Clay, No. 4

The hand specimen and outcrop are slightly tan-colored whitish, weakly schistose clay that breaks to angular and sub-angular coarse fragments.

In thin section, plain light, No. 4 shows less iron oxide, and more abundant quartz than did No. 3; some schistosity continues.

Between crossed polars, interference colors are lower than in No. 3., and the clay particles are finer and tend to be more platy. The plates are roughly parallel to the schistosity that is preserved by the iron-oxide flecks.

In the X-ray diffractogram, kaolinite is recorded by strong 001 (7.12 Å) and 002 peaks but prism reflection bands are very weak. Quartz is shown more strongly in No. 3 than it is in No. 2.

*First-quality Refractory Clay, No. 5, and Selected
High-refractory Quality No. 5X*

Both clays are slightly tan, fairly soft, and friable. Although faint parallelism remaining from the schist is observable in many clay lumps, they fracture in random directions.

The thin sections in plain light show two phases, (1) mostly "clear" clay mineral, through which is distributed (2) many tiny, thin, slightly elongate flecks or shreds of iron oxide in sub-parallel arrangement remnant of the schist.

Between crossed polars the clay mineral crystals are first-order dark grey in interference color, interlocking, anhedral, and range in size from 20 to 40 microns in cross section. Upon insertion of a first-order red plate, alternate yellow or blue interference color dominance (estimated 3 : 2, instead of 1 : 1 as would occur in random orientation) is seen in the 45° extinction positions, thus indicating parallel orientation of clay mineral crystals. The color produced by oriented clay is somewhat reduced by the presence of quartz (calculated nearly 25%, from chemical composition) which occurs in random orientation. Coarse pseudomorphs (?) 0.08 to 0.12 mm in cross-section, of clay after feldspar grains show undulatory extinction independent of the schistose orientation. Veinlets of kaolinite, in which the clay plates tend to lie parallel to the walls, cut across the schistosity. Occasional veinlets of fine to microcrystalline quartz crystals in random optical orientation are aligned with the schistosity.

The pronounced orientation of the bulk of the kaolinite crystals parallel with the foliation of the chlorite schist was checked independently by X-ray diffraction. Equal-area wafers of clay were cut parallel and perpendicular to the relict schistosity in a clay sample altered from a chlorite schist zone, and mounted surface-flush in slots of regular X-ray sample holders. The basal reflections were 1.6 to 2 times higher in the "parallel" than in the "perpendicular" cut; these differences were noticed in both room-dry and glycolated samples, Fig. 1. Presumably the orientation of oxygen sheets in the chlorite was "remembered", or transferred to oxygen sheets of kaolinite.

The mineral composition of the 5X sample may be calculated from its chemical analysis, Table 1, by allotting all Al_2O_3 to kaolinite. As a check on its validity, the loss on ignition if taken as $\text{H}_2\text{O}+$ is accounted for stoichiometrically. After necessary SiO_2 is allocated to kaolinite (72%) an excess of 23.6% SiO_2 is left as quartz, Table 2.

The X-ray diffractogram of No. 5 shows strong 001 and 002 reflections of kaolinite and very weak, unresolved bands from prism reflections, similar to those of G-10 in Fig. 1. In no. 5X the prism band is noticeably stronger than in No. 5, but is still relatively unresolved, and quartz reflections are only half as intense as in No. 5. Thus, last-stage leaching (a purification) of the clay removed quartz and promoted crystal growth and recrystallization of kaolinite.

Clay from sample 5X was treated (intersalated) with KOAc, which yielded

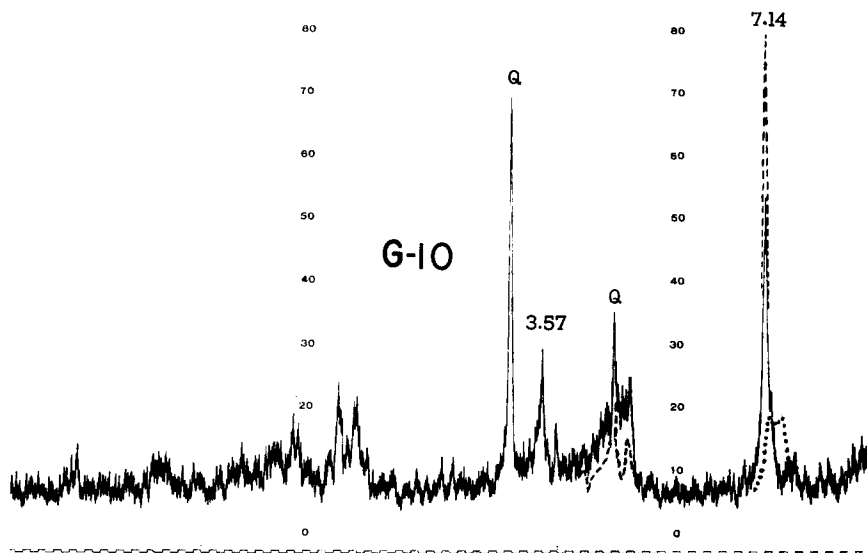


FIG. 1. Composite X-ray diffractogram of Guanajuato kaolin, G-10, from a zone of former chlorite schist. The continuous line is the original instrumental record of a clay sample cut perpendicular to the schistosity. The dashed line is an added trace from clay cut parallel to the schistosity, showing a higher basal reflection, but weaker prism reflections. The dotted line shows the blunted basal peak of clay 5X after treatment with KOAc and ethylene glycol. Cobalt radiation.

TABLE 2.—
CALCULATED MINERAL
COMPOSITION OF No. 5X

72.0	kaolinite
23.6	quartz
1.54	TiO ₂ , anatase (?)
0.6	Fe ₂ O ₃ hematite
1.25	CaO — 2.2% CaCO ₃ (?)
<hr/>	
98.99	

a sharp 13.8 Å peak. Washing the clay with water and ethylene glycol, following the procedure of Miller and Keller (1963), completely removed the 14 Å reflection and replaced it with a sharply blunted basal peak whose top extends across 7.2 to 7.62 Å, Fig. 1. This broad reflection is interpreted as coming from a randomly interstratified mixture of kaolinite with an expansion-susceptible, hydrated progenitor.

CHEMICAL CHANGES DURING ARGILLATION

Chemical changes undergone by the rocks during argillation may be traced *trendwise* by comparing analyses (Table 1) of rocks collected sequentially. Precise changes, however, in individual chemical elements may not necessarily be evaluated by such comparison because, as in this study, it is not known whether, or not (but probably not), the composition of the unaltered antecedent of No. 3 was exactly the same as those of Nos. 2 and 1, etc.

Ignition loss tended to increase, from 8 to 10%, during argillation. The increase is probably real, but not large because of the presence of OH-containing chlorite, hornblende, and epidote in the fresh rock.

SiO₂ increased notably, from 45.7 to 62.6% from Nos. 1 to 4. An increase in SiO₂ is usually not expected during the kaolinization of an igneous or metamorphic rock. The increase in this sequence is caused by the introduction of quartz, most of which is so fine grained as to be scarcely identifiable with the microscope but is detected with X-ray. Last-stage hydrothermal action dissolves SiO₂, following initial kaolinization, as shown by a 5% decrease in No. 5X. At other field localities, analogous introduction of SiO₂ followed by dissolution has been observed.

Al₂O₃ shows a monotonic increase during argillation, although high Fe₂O₃ in No. 2 substitutes in part for Al₂O₃. Ferrous iron is oxidized prominently at the outset and continues to decrease.

Mg shows prompt dissolution in the first stages, which is typical of the usual mobility of Mg.

Ca dissolution was scanty until argillation of the feldspar occurred, as in the stage represented by sample No. 3.

Na dissolution occurred prior to that of Ca because Na was essentially gone at argillation stage No. 3.

K, Mn, and P were insignificant in quantity, and TiO₂ remained relatively unchanged.

Generalizing on the chemical changes, the first effect was oxidation of iron, loss of Mg, and partial dissolution of Na. Argillation then began, and continued with dissolution of Na and Ca, and translocation of silica with deposition of fine-grained quartz. "Homogenization" of the rock occurred as the coarser-grained metal-cation minerals were altered to fine-grained, uniform-textured, H-cation kaolinite. After kaolinization, part of the quartz was dissolved.

We envisage that, in the field, hot fluids rising along fractures encountered otherwise descending phreatic and oxygenated meteoric water, and recirculated them upward and outward. Oxidation of the rock began first near the fractures and moved outward as a wave. Behind this front, the oxidation gave way very gradually to a zone dominated by leaching and that, in turn, graded into argillation (nearest the fracture). Thus oxidation, leaching, kaolinization, and dissolution of finely crystalline quartz nearest the fracture, were carried on simultaneously—not as independent episodes. The chemical system was obviously open.

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