Clays and Clay Minerals, 1969, Vol. 17, pp. 9–12. Pergamon Press. Printed in Great Britain

HYDROTHERMAL ARGILLATION OF VOLCANIC PIPES IN LIMESTONE IN MEXICO

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(*Received* 25 *September* 1968)

Abstract – Previously reported deposits of kaolin of hydrothermal origin in Mexico have been described from igneous parent rocks dominantly extrusive in occurrence. Recently observed evidence from other localities confirms an intrusive mode of occurrence, however, for hydrothermally kaolinized agglomerate and tuff within limestone host rock. Three such occurrences have been recognized near Jasso-Calera, north of Mexico City, and near Coacoyula, Guerrero, and Sombrerete, Zacatecas.

The contacts of these clay deposits with limestone show regularly a concentration of iron-rich minerals such as red to brown oxides and/or nontronite, but less commonly an irregular development of grossularite, and bands or pockets of endellite. Silica gossans indicate that hypogene altering solutions were active into the current geomorphic cycle. Kaolinite at the center of the clay body and endellite at the border zones are interpreted as originating, respectively, from *in situ* alteration of solid rock and deposition from ambient solutions.

INTRODUCTION

THE IGNEOUS rocks which are parent to most hydrothermally formed commerical refractory clay deposits in Mexico are commonly extrusive, such as perlitic rhyolite (Keller, 1963), numerous lava flows, and volcanic breccia (Keller and Hanson, 1968). Recent observations, however, have confirmed that volcanic breccia in pipes and fills within limestone country rock were kaolinized at three localities separated as much as 1000 km. air distance. They occur at Jasso-Calera, near Coacoyula (and Iguala) in northern Guerrero, and near Sombrerete, Zacatecas, Fig. 1. These localities have been productive clay occurrences for some time, but the geologic relationships of clay to country rock remained equivocal until

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Fig. 1. Index map of clay deposits.
1. Jasso-Calera (near Tula), Hidalgo.
2. Sombrerete, Zacatecas.
3. Coacoyula (near Iguala), Guerrero.

https://doi.org/10.1346/CCMN.1969.0170103 Published online by Cambridge University Press

recently (1968) when some exposures and contacts of geologically critical importance were bared and studied. Jasso-Calera best shows the physiographic and spatial distribution of volcanic vents and shattered country rock, Sombrerete shows the contact zone, and Coacoyula adds confirmation to evidence observed at the other two locations.

JASSO-CALERA DISTRICT

About 75 km north and slightly west from Mexico City, toward Tula, via Mexico Highway 57, is the Jasso-Calera silica and refractory-clay producing district, named from nearby towns. The country rock is bluish gray Cretaceous limestone that has been faulted and tilted as much as 90°, and highly fractured, especially near the volcanic pipes which later were altered to clay. The limestone is being quarried for large-scale use in Portland cement.

Some 20 large exposures of clay, argillized silicate rock, or silica (quartz) rock, that stand about 200 m above the valleys, are distributed on a prominent N–S trending limestone ridge 10–15 km long. These silicate areas, bared by erosion or by quarrying, are roughly circular to oval in ground pattern, ranging up to about 100 m in diameter, of which 30–50 m diameters are more common. These are volcanic pipes which have penetrated the limestone, highly brecciating it around the pipes. Breccia fragments, boulder to gravel size, are well recemented and healed except for some partially rounded limestone boulders a meter, more or less, in diameter, remaining free standing in the walls of the pipes. No identifiable corrosion of limestone by lava has been observed. Most of the filling of the pipes is by pyroclastic material, some of which has preserved relic structure where argillation has not been complete. It is likely that these pipes were the vents through which was erupted volcanic debris scattered about the region and partially filling nearby valleys undergoing stream erosion.

Silica (quartz and chalcedony) gossans up to about 3 m thick cap the larger pipes. Some of this material is being produced for grinding media and silica refractories. Typically, the silica rock grades downward into less silicified volcanic rock which, in turn, may merge downward into kaolin commonly admixed with alunite. A prospect hole in one of the pipes has confirmed kaolinization to a depth in excess of 100 m.

The argillation at depth, plus the silica gossan, confirms that the argillizing fluids were rising, presumably warmed by heat introduced during the volcanic process. The silicified surface rocks being an integral part of the geomorphic surface, and likewise gradational with the rocks below, date the time of silicification and argillation within the geomorphic cycle that extends into the present.

As a clay deposit is mined toward its edge, almost invariably a clue to proximity of the contact with limestone comes from abrupt, high increase in red to brown iron oxide in the clay. Likewise, the clay may also change from 1 : 1 to 2 : 1 in structure, and silica content (either free or combined) may increase, but appearance of "irony" clay almost always warns of approach to limestone. Similarly, at San Louis Potosi, where rhyolite breccia was kaolinized and at Guanajuato, where hornblende-chlorite schist was similarly argillized, iron in the parent rock was observed (Keller and Hanson, 1968) to have been alternately mobilized, dissolved, and reconcentrated as oxide on both microscopic and macroscopic scales at or near the reaction zone of clay with "rock"-- although not with the intensity of concentration it shows near a contact with limestone. These observations suggest that limestone wall rock has greater chemical effects – whether due to Ca ions, pH, or pE (increasing oxidation) is not known – in inducing the deposition of red–brown iron oxide than are the effects arising from silicate wall rocks.

Prominent slickensiding is commonly developed at clay limestone contact zones, usually in the clay portion, or on clay-coated limestone surfaces. The movement which is recorded by the slickensides may have been due to sliding during eruption, or alternatively to subsidence due to volume reduction that occurs in the parent silicate rock as a result of desilication.

Desilication of rhyolite containing 70–72 per cent silica and 16–17 per cent alumina to kaolin clay containing 35–40 per cent alumina results in a net loss of about 50 per cent by weight. However, because bulk specific gravity is simultaneously reduced from about 2·3 (rhyolite) to 1·8 (San Luis Potosi kaolin), volume reduction going from rhyolite to kaolin should be about 20–25 per cent. In the case of unaltered tuff and related pyroclastics having lower bulk specific gravities than rhyolite, the volume reduction going from tuff to kaolinite is probably of the order of only about ten per cent. Possibly such volume shrinkage may be taken up by movement marked by slickensiding along the periphery and fracture zones and at internal adjustments within hydrothermal clay bodies.

CLAY-LIMESTONE CONTACT ZONE AT SOMBRERETE, ZACATECAS

A contact zone between limestone country rock and kaolin, permitting close examination of those relationships, was exposed during one phase of the mining operations at Sombrerete. Otherwise, the general geology is much the same as at Jasso-Calera.

The limestone country rock at Sombrerete was thoroughly fractured to boulder and gravel sizes. The original limestone was probably a micrite, which has undergone some recrystallization to a coarser texture of subhedral to anhedral, usually clouded, carbonate grains. Tiny rounded ovals, near-spheres, and cubes (?) with subrounded edges and corners are scantily distributed here and there in thin section of the rock. In transmitted light the smallest are brown; the cubes (?) were probably pyrite that is now oxidized. Fracture fillings that cement the brecciated particles consist of relatively clear spar in coarser, commonly pressure-twinned crystals mixed with darker, fine-extured remnants (?) of original limestone. The limestone face at the exposed contact zone with clay is generally smoothed, slickensided, and thinly coated with a fine, greenish powder.

This powder occurs in a zone about 15 cm wide. It is friable to loose, greenish-gray, fine-sand to silt size material that first was incorrectly interpreted in the field as fault gouge. Microscopic examination and X-ray diffraction show this "sand" to be composed of grossularite and quartz. In transmitted light it is rather darkly clouded, due probably to the effect of a high index of refraction (1·740), although the particles are clear to white in reflected light.

Grossularite indicates, obviously, that a high-temperature metamorphic reaction occurred at some of the intrusive contact surfaces. At other deposits, for example at Jasso-Calera, the contact rocks contain calcite, kaolinite, quartz, and dolomite, in order of decreasing abundance. Apparently the temperature of intruding pyroclastics was too low here to cause the tuff to react with the carbonate country rock.

From the grossularite-quartz zone toward the clay deposit, at Sombrerete is a vertical endellite-dominant zone averaging about 1 m in width. It is divided into four distinct vertical color bands separated by partings. Band "*a*", next to the grossularite-quartz zone, is 3–10 cm wide and consists of waxy, greenish brown endellite (10 Å, 001 spacing) heavily pigmented with purple to black dendritic and spotty mottling. The clay, some of which is partly silicified, breaks with small conchoidal surfaces. Band "*b*" (towards the clay deposit), varying in width from 15–30 cm, is tan–light greenish-brown, waxy, irregularly-fracturing endellite. Slicken-siding is abundant in this zone. It is only scantily silicified. Band "*c*", characterized by vivid red–brown coloured endellite, narrows and widens from 10–25 cm. It includes a few sporadic, angular, pebble-size fragments of white kaolinitic clay such as comprises the main body of the clay. It is not known whether these white lumps were fragmented and included in the red band after the time of major kaolinization or whether they represent kaolinized angular pyroclastics whose fragmentation predates the kaolinization. Band "*d*", separating "*c*" from the main white clay body, varies from dark brown to purple clay. It may be 5–15 cm. wide, or be cut out entirely by expanded width of band "*c*". This zone grades into the merchantable kaolin of the main body.

Bands "*b*", "*c*", and "*d*" derive their vivid colors from abundant iron oxide. They constitute the "irony clay" zone that characterizes the contact of hydrothermal clay and limestone in Mexico, and warn the miner of proximity to the wall. They are the analogs of the iron-mobilized and iron-rick bands in clay deposits where the country rock is volcanic flow rock. At still another contact zone at Sombrerete the iron resides in waxy green expanding clay (when treated with glycol), presumably nontronite.

The major clay mineral at the Sombrerete locality is moderately well ordered kaolinite, but minor endellite, translucent to iron-oxide stained, occurs here and there in the deposit, particularly near its margins. What was the cause for differentiation in kaolin mineral species between the body of the clay deposit and its peripheral envelop? An answer at this time is speculative only, although it is consistent with the history of the agrillation.

Following the eruption of rock-forming materials, which left the feeder pipes filled with volcanic aggolmerate and ash, rising solutions desilicated and argillized these rocks. Kaolinite was the dominant clay mineral formed from the solid silicate rocks. It appears to us that the continual presence of parent silicate rock which kept the reacting system saturated with ions being removed from the rock may have been significant to cause kaolinite to be formed. That is, in effect the kaolinizing system was maintained as "saturated with parent rock," or in other words, the "activity of parent silicate rock was 1·0".

At border zones, however, endellite was deposited from the dissolved load of solutions that had moved outward beyond the environment where Al and Si ions could be replenished from nearby pyroclastics. Deposition of the endellite from these solutions probably was caused by lowering of temperature (effects of cold country rock), reaction with ions from the limestone, or both. Thus the basic energy changes causing deposition would be decidedly different between kaolinite-replacing and endellite-producing systems.

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Résumé—De gisements déjà découverts de kaolin d'origine hydrothermique au Mexique ont été décrits; ils proviennent d'une roche de départ ignée et surtout extrusive. Pourtant sur la base des observations récentes dans d'autres endroits, on a l'impression d'une origine intrusive de l'aggloméré kaolinisé de manière hydrothermique et du tuf dans une roche de départ calcaire. On a reconnu trois formations de ce genre près de Jasso-Calera au nord de Mexico City, et dans la région de Coacoyula, Guerrero, et Sombrerete, Zacatecas.

Les contacts entre ces gisements d'argile et la roche calcaire montrent régulièrement une concentration de minéraux à forte teneur de fer, p.e. les oxides rouges ou bruns et/ou le nontronite, mais de manière moins commune un développement irrégulier de grossularite, et des bandes ou poches d'endellite. Les gossans de silice montrent que des solutions modifiant l'hypogène étaient actives dans le cycle géomorphique actuel. Le kaolinite au centre de l'accumulation d'argile et l'endellite aux zones marginales sont censés avoir leur origine respectivement dans l'altération *in situ* de la roche solide et dans la déposition à partir des solutions environnantes.

Kurzreferat—Kaolinablagerungen hydrothermischen Ursprungs in Mexiko, über die bereits früher berichtet wurde, sind als Massengestein von vorherrschend extrusivem Zustandekommen beschrieben worden. Vor kurzem beobachtetes Material von anderen Orten bestätigt jedoch die intrusive Ablagerung von hydrothermisch kaolinisiertem Agglomerat und vulkanischem Tuff innerhalb eines Kalkmuttergesteines. Drei solche Vorkommen sind in der Nähe von Jasso-Calera im Norden von Mexico-City und in der Nähe von Coacoyula, Guerrero sowie Sombrerete, Zacatecas festgestellt worden.

Die Berührungsstellen dieser Tonablagerungen mit Kalk weisen regelmässig eine Konzentration eisenreicher Minerale wie roter bis brauner Oxyde und/oder von Nontronit, jedoch weniger häufig eine unregelmässige Entwicklung von Grossularit, und Bänder oder Nester von Endellit auf. Silikahaltiger eisenschüssiger Letten deutet darauf hin, dass hypogene Verwandlungslösungen in den gegenwärtigen geomorphischen Zyklus hinein wirksam waren. Das Vorkommen von Kaolinit im Inneren des Tongesteines von Endellit in den Grenzzonen wird auf Veränderung des Festgesteins an Ort und Stelle bzw. auf Ablagerungen aus umlaufenden Lösungen zurückgeführt.

Резюме—Образование известных гидротермальных месторождений каолина в Мексике связывается с изменением изверженных пород, преимущественно экструзивных. Приводятся новые данные о гидротермально каолинизированных агломератах и туфах, залегающих в известняках в Хассо-Калера (севернее города Мехико), а также в окрестностях Коакоюла (штат Герреро) и Сомбререте (Закатекас).

Для контактов глин с известняком характерна концентрация обогащенных железом минералов—красных до бурых окислов железа и/или нонтронита, реже гроссуляра; наблюдаются также выделения галлуазита. Каолинит в центральной части залежи и галлуазит в ее краевых частях рассматриваются как образовавшиеся соответственно in situ (путем замещения) и путем отложения из растворов.

https://doi.org/10.1346/CCMN.1969.0170103 Published online by Cambridge University Press