

INIGUEZ-  
3

# DEVELOPMENTS IN SEDIMENTOLOGY

35

H. VAN OLPHEN  
F. VENIALE  
(EDITORS)



BIBLIOTECA  
11 OCT. 1985

**INTERNATIONAL  
CLAY CONFERENCE  
1981**

ELSEVIER

## BASALTIC AND RHYOLITIC ROCKS AS PARENT MATERIALS OF HALLOYSITE IN ARGENTINE DEPOSITS

A. M. INIGUEZ RODRIGUEZ

Centro de Investigaciones Geológicas  
Universidad Nacional de La Plata - CONICET  
1900 La Plata, Argentina

### ABSTRACT

In northeastern Argentina there is a vast area of deeply weathered tholeiitic basalts of Cretaceous age. Studies based mainly on X-ray diffraction, electron microscope and chemical analyses have shown that zeolites and montmorillonite are formed at depth while halloysite and kaolinite associated with gibbsite and iron oxides occur near the surface. Halloysite is abundant at the contact between weathered basalt and soil (oxisol) and decreases towards the surface where kaolinite predominates.

On the other hand, rhyolitic vulcanites and ignimbrites of the Jurassic, Bahia Laura Group, outcropping in Patagonia have undergone weathering and hydrothermal alteration forming halloysite and kaolinite with abundant silicification and transformation of biotite into hydrobiotite. These processes have produced important clay deposits in the provinces of Chubut and Santa Cruz.

In the case of the basalts, halloysite is derived by weathering action on labradorite, while in the case of the rhyolites it is produced by hydrothermal action on sanidine. Operations to beneficiate the Chubut and Santa Cruz kaolins are necessary for applications other than ceramics.

### INTRODUCTION

Two major areas of basaltic and rhyolitic rocks provided the parent materials for the formation of halloysite ( $7\text{\AA}$ ). One of these areas is

located in northeastern Argentina, on the border of Brazil and Paraguay (Fig. 1), where cretaceous tholeiitic basalts outcrop, which have been deeply weathered, to form clayish red soils (oxisoils). The relief is slightly undulating, cut by the Paraná and Uruguay Rivers. The annual rainfall averages 1.755 mm and temperatures are between 39.6°C in summer and below 0°C in winter.

The basalts are typically flow-banded. Bands consist of vesicular and massive basalt flows, varying in color from dark gray to reddish gray and grayish green. Intergranular and hyaloophitic textures are common in vesicular basalts, while intergranular and subophitic textures are present in the massive varieties.

Optical microscopy (Teruggi 1955; Iñiguez 1978), indicates that plagioclases are the dominant constituents, as randomly oriented, well developed tabular crystals, with slightly altered edges. The composi-



Fig. 1. Map showing the location of the study areas.

tion corresponds to labradorite ( $An_{50} - An_{65}$ ). The second mineral in importance is augite, with prismatic or granular habit, and associated with minor amounts of pigeonite and diopside.

Opaque minerals are abundant, occurring as large crystals or small granular aggregates of magnetite and hematite. Only a trace amount of volcanic glass remains as interstitially, deeply altered clay products. Accessory olivine, apatite and zircon have been observed.

Surface weathering has deeply altered these basalts (Riggi *et al.* 1964), leading to the formation of clayish red soils (oxisoils), which are spread over an extensive area.

A cross section of deeply weathered basalt to the soil zone, developed in situ, shows a distinctive mineralogical zonation (Fig. 2) Halloysite ( $7\text{\AA}$ ) is the dominant clay mineral in the limit between the deeply weathered basalt and the soil zone.

The second area previously mentioned, is of greater importance and comprises volcanic outcrops of the Serie Tobifera (Bahía Laura Group),

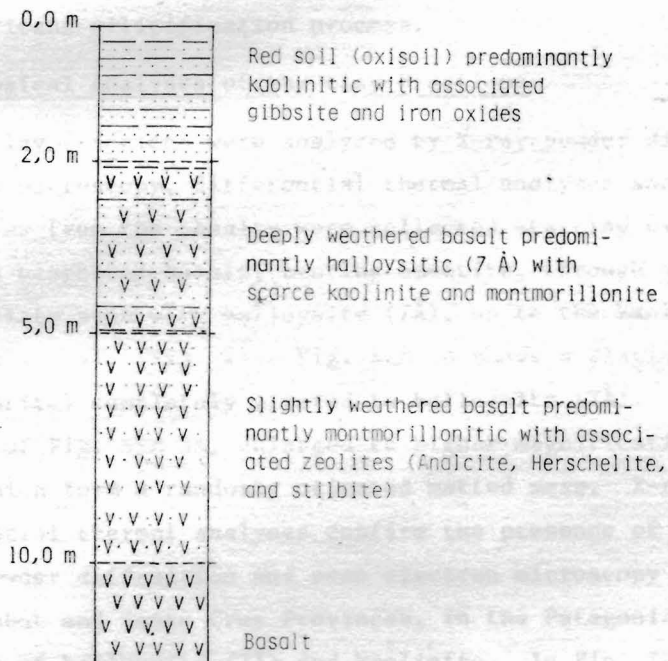


Fig. 2. Diagrammatic section showing grading alteration.

in the Patagonia Argentina (Fig. 1).

Climate is arid and cold, the annual rainfall averages 223 mm and the mean annual temperature is 9°C. Topographically, the area is a peneplain, with several rivers running in a west-east direction such as the Chubut and Santa Cruz Rivers, and others.

These volcanic rocks, Jurassic in age, (Feruglio 1949), are for the most part rhyolites and ignimbrites, which by weathering and hydrothermal alteration formed secondary kaolin deposits (Hayase, K y Maiza 1969-1970) and (Romero, A. *et al.* 1975), which are mainly halloysitic. Petrographically, porphyritic rhyolitic rocks contain well developed quartz, sanidine and biotite crystals. Euhedral quartz crystals are dominant, showing corrosion effects, embayments and secondary growths of abundant euhedral phenocrystals of typically twinned sanidine, also showing corrosion effects and embayments. Sanidine usually alters to halloysite (7Å), and kaolinite. No plagioclases were detected. Biotite alteration to hydrobiotite was frequently observed.

The ground mass has a felsitic to microgranular texture indicating a significant silicification process.

#### Mineralogical Analyses of the Clay Fractions

The clay fractions were analyzed by X-ray powder diffraction, scan electron microscopy, differential thermal analyses and chemical analysis.

Samples from the basalts were collected starting with the fresh slightly weathered basalt, bearing smectite, through a deeply weathered intermediate zone with halloysite (7Å), up to the kaolinitic red soil zone (oxisols), (Fig. 2). Fig. SEM 3A shows a plagioclase crystal (labradorite) completely altered to halloysite (7Å). Fig. 3B is a view of part of Fig. SEM 3A, enlarged to higher magnification, and shows tubes which form a randomly oriented matted mass. X-ray patterns and differential thermal analyses confirm the presence of halloysite (7Å). X-ray powder diffraction and scan electron microscopy of clay deposits from Chubut and Santa Cruz Provinces, in the Patagonia region, show the presence of halloysite (7Å) and kaolinite. In Fig. SEM 4A and SEM 4B (suspension in water), mixtures of the two minerals can be seen.

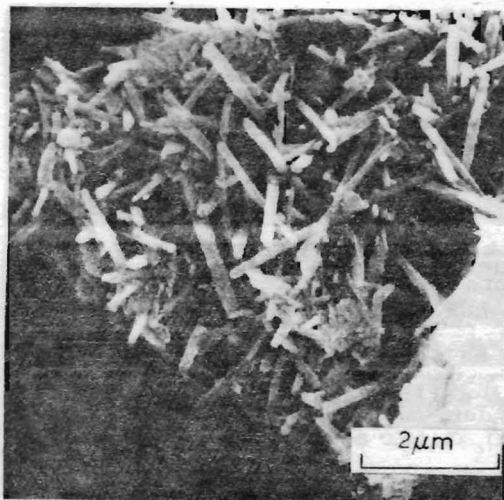


Fig. 3A. Matted fibers of halloysite tubes randomly oriented growing up from plagioclase crystals in basalts.

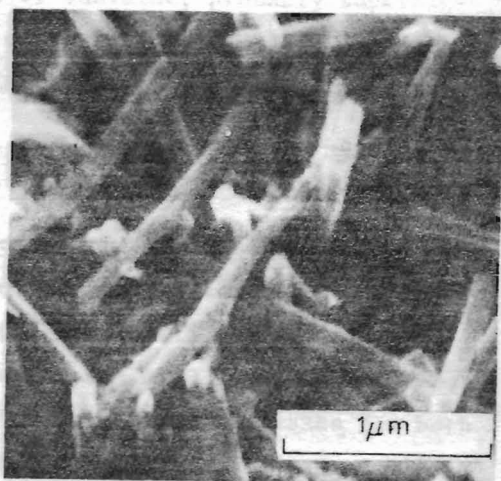


Fig. 3B. Views of part of Fig. 3A with higher magnification.

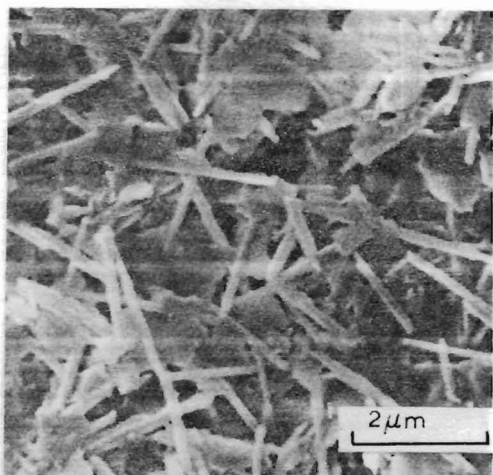


Fig. 4A. Subhedral kaolinite flakes and halloysite elongates in rhyolites.

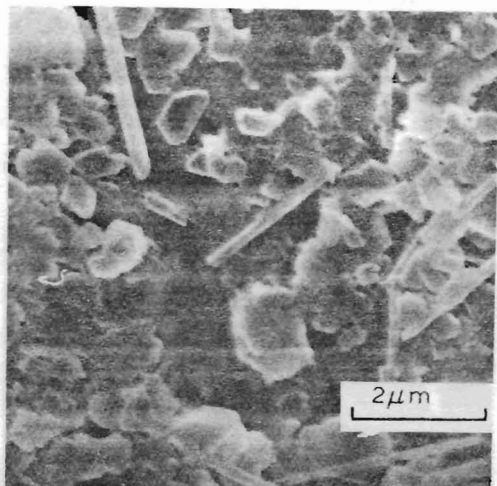


Fig. 4B. Subhedral hexagonal flakes of kaolinite prevailing over halloysite (7 Å) tubes in rhyolites.

Allophane was not observed. Crystals of sanidine, probably superficially altered to halloysite ( $7\text{\AA}$ ) are commonly observed (Fig. SEM 5A) and bipyramidal volcanic quartz crystals ( $10\ \mu\text{m}$  long), are important components (Fig. SEM 5B).

### Chemical Analyses

Fig. 6 is a diagrammatic presentation of the results of chemical analyses of the fresh basalts and rhyolites on the left, and of the oxisoils and kaolinized rhyolites on the right. The compositions are in general quite similar: silica decreases and  $\text{Al}_2\text{O}_3$  increases for both. In basalts,  $\text{FeO}$  decreases and  $\text{Fe}_2\text{O}_3$  increases;  $\text{TiO}_2$  increases for both and alkaline earths and alkali content, all decrease with a notable decrease of the  $\text{CaO}$  and  $\text{MgO}$  contents for the basalts and of  $\text{K}_2\text{O}$  for the rhyolites.  $\text{MnO}$  decreases slightly in the basalts and remains constant in the rhyolites. A similar behavior has been reported by Murray (1978) for the alteration of a granite to kaolin.

### Genesis of Halloysite

Weathering of basaltic rocks, as a result of movement of rain water

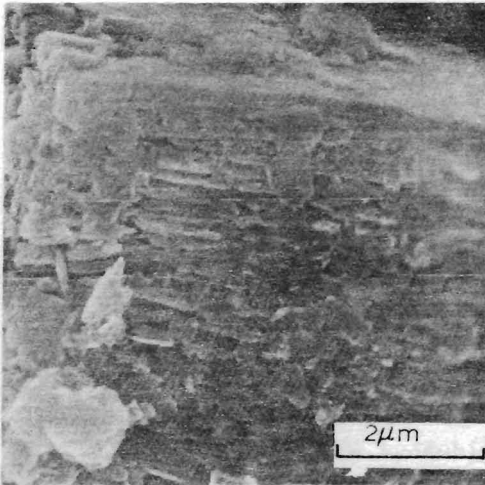


Fig. 5A. Altered sanidine crystal leading to the formation of halloysite ( $7\text{\AA}$ ).

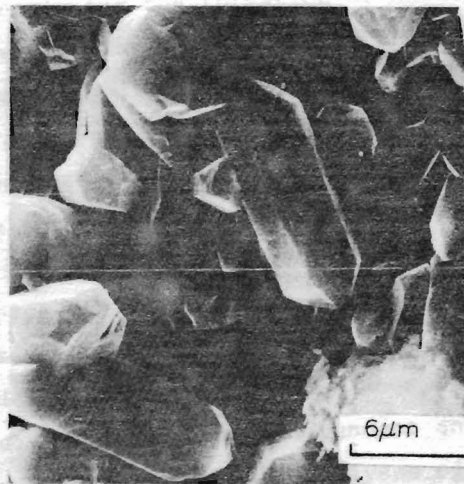


Fig. 5B. Fine grained bipyramidal volcanic quartz crystals.

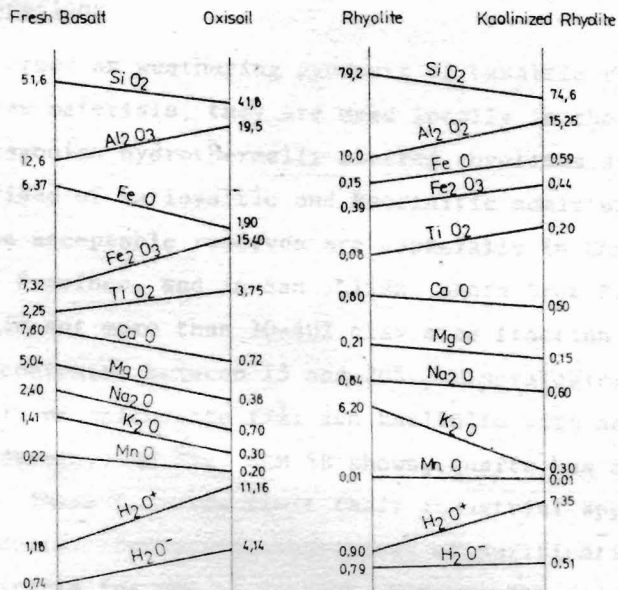


Fig. 6. Diagrams showing chemical analysis of fresh rocks (left) and kaolinized rocks (right).

through the rocks, was evidently responsible for the alteration of feldspars (labradorite) and consequently for the formation of halloysite (7Å). This process occurs less with increasing depth. Chemical analyses of fresh and weathered basalts (soils), show various changes of composition as a result of alteration processes. From SEM evidence, halloysite seems to have transformed into kaolinite towards the top zone. Formation of gibbsite, as well as concentration of iron oxides, are also significant.

According to field and petrographical observations, the formation of halloysite in rhyolitic rocks is due to hydrothermal alteration of sanidine. Parallel bands of well defined alteration zones show that biotite has changed to hydrobiotite. Silica veins are abundant and feldspars (sanidine) are completely altered. Chemical analyses of fresh and weathered rhyolites confirm the occurrence of this process, which was responsible for the formation of residual and sedimentary

deposits in the Patagonia Argentina.

### Economic Implications

Red soils formed as weathering products of basaltic rocks are not high quality raw materials, they are used locally in the red brick industry. Patagonian hydrothermally altered rhyolites are important deposits comprised of halloysitic and kaolinitic admixtures with good whiteness. The acceptable reserves are especially in Chubut River Valley, Chubut Province, and in San Julián, Santa Cruz Province. These deposits contain not more than 30-40% clay size fraction ( $<4 \mu\text{m}$ ) with varying  $\text{Al}_2\text{O}_3$  contents, between 15 and 20%. Mineralogically they consist essentially of halloysite ( $7\text{\AA}$ ) and kaolinite with associated quartz and feldspars. As Fig. SEM 5B shows, quartz has a very small particle size. These features limit their industrial applications to white ware products. Processing operations of purification could make these clays suitable for use as fillers; but not for paper coatings because of the high content of halloysite and fine particle quartz.

### REFERENCES

- Feruglio, E., 1949. Descripción geológica de la Patagonia. Dirección de YPF. Bs. As. Argentina.
- Hayase, K. y Maiza, P., 1969. Génesis del Yacimiento de caolín de la mina Villegas. Prov. de Chubut, República Argentina, Rev. Assoc. Geol. Arg., XXIV, 1, 65-71, Buenos Aires.
- Hayase, K. y Maiza, P., 1970. Génesis del yacimiento de caolín de la mina Eguivocada, Provincia de Chubut, República Argentina, Rev. AMPS, 1, 1-2, 33-47, Buenos Aires.
- Itziguez, A. M., 1978. Los minerales secundarios y su influencia en el comportamiento geotécnico de los basaltos del Río Uruguay. Area de Garruchos-Garabí (Provincia de Corrientes), República Argentina. Obra del Centenario del Museo de La Plata, Tomo IV, 137-151. La Plata.
- Murray, H. H., 1978. Alteration of a granite to kaolín. Mineralogy and geochemistry. Schriftenr. Geol. Wiss. Berlin, 197-208.
- Riggi, J. C. y Feliu de Riggi, N. A., 1964. Meteorización de basaltos en Misiones. Rev. Asoc. Geol. Arg. XIX, 1, 57, 70, Buenos Aires.
- Romero, A., Dominguez, E. y Whewell, R., 1975. Génesis de los yacimientos de Caolín del Río Chubut inferior. II Congr. Iberoamericano de Geología Económica. V, 423, Buenos Aires.
- Teruggi, M. E., 1955. Los basaltos tholeiíticos de Misiones. Notas Museo de La Plata. XVIII, Geol. N° 70, 259-278. La Plata.