

HALLOYSITE-KAOLINITE TRANSFORMATION AT ROOM TEMPERATURE

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(Received 8 June 1974)

Abstract—Halloysite (metahalloysite) of various particle sizes has been altered with oxalic and EDTA acids, at room temperature and during different periods of time (5–90 days). The oxalic acid attack at first achieved only a recrystallization of halloysite. The recrystallization is much more significant the smaller the size of the treated halloysite particles. Later the material is destroyed. The EDTA treatment also has provoked during the first days a recrystallization of the halloysitic material which is destroyed again after about 20–25 days. Later kaolinite is formed. The kinetic curve of kaolinite formation is symmetrical with respect to that corresponding to the diminution of amorphous material in the sample. The influence of the halloysite particle size and the complexing effect of the acids in relation to the resulting products are discussed.

INTRODUCTION

The transformation of halloysite to kaolinite at room temperature is theoretically possible, since halloysite is metastable with respect to kaolinite. The free energies of formation of these minerals (Hem *et al.*, 1973) are, respectively:

$$mG_f^0 H \geq -898.4 \text{ kcal/ml}$$

$$\Delta G_f^0 K = -902.9 \text{ kcal/ml.}$$

The difference between them logically favors the transformation of halloysite to kaolinite.

In *Nature*, such a transformation was proved by Tamura and Jackson (1953), who established that in certain kaoliniferous soils formed from feldspathic rocks, there existed a successive sequence of transformations from feldspar to kaolinite, passing through amorphous stages (allophanes), hydrated halloysite and metahalloysite. Subsequently, Kinoshita and Muchi (1954), Fieldes (1955), Sudo and Takahashi (1956), Ponder and Keller (1960), Keller (1964) and Chen (1969) among others, upon studying different processes of kaolinization, have found transformations of halloysite to kaolinite, especially under weathering conditions.

These transformations have been observed also in some Spanish kaolin deposits by Galan and Martin Pozas (1971), Martin Pozas *et al.* (1971), Galan (1972) and Galan and Martin Vivaldi (1973), appearing in some of these deposits sequences more or less complete from K-feldspar, or Na-plagioclases, to ordered kaolinites, through aluminium oxides, allophanes, hydrated halloysite, metahalloysite and disordered kaolinite.

The experimental transformation of halloysite to kaolinite at room temperature has not been undertaken until now. In this paper, we present the results of the alteration at room temperature of halloysite

with oxalic and ethylenediamine tetra-acetic acids in which processes kaolinite has been obtained.

MATERIAL AND METHODS

The alteration with oxalic acids and EDTA has been carried out over Eureka halloysite (API, No. 16) that is essentially composed of metahalloysite, with illite and quartz as impurities.

The halloysite has been subjected previously to a prolonged dry grinding in a Glen Creston mixer mill with a polystyrene cylindrical vial with covers of wolfram carbide and balls of the same material, for the purpose of obtaining small-sized particles, which have been controlled by X-ray diffraction according to the methods of Scherrer (in Klug and Alexander, 1954), and using the 02 band (4.43 Å),

$$\text{In the equation: } D_{0k} = \frac{K}{B \cos \theta}$$

K is the so-called 'form factor' and according to Klug and Alexander (1954) its value is 1.84 for a 0k band according to Brindley and Robinson (1948), λ is 1.54 Å (Cuk α -radiation) and B is the half-maximum line breadth.

To the value calculated directly for B it is necessary to subtract the width of the peak which, for the angle considered, involves the diffractometer used. This value has been calculated using well-crystallized quartz (2–20 μm size), measuring the width of the reflections at 4.26, 3.34 and 1.82 Å and deducing from them those corresponding to the 4.42 reflection, calculated by extrapolation.

The distribution of the halloysite particle size as a function of the grinding time is shown in Table 1. Nevertheless, such calculated values are less than the real ones, since for their determination we have used the reflection at 4.43 Å, which presents a band

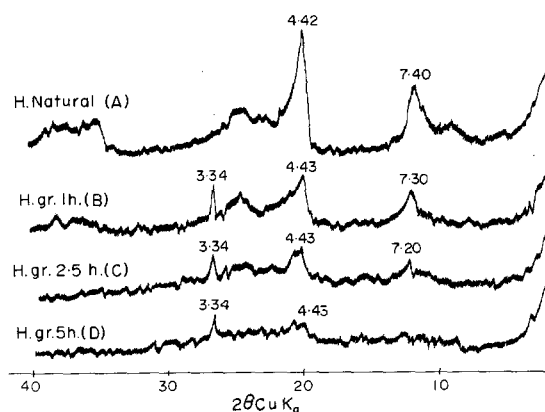


Fig. 1. X-ray diffraction patterns of natural halloysite (fraction A), and halloysite ground for 1, 2.5 and 5 hr (B, C and D fractions, respectively).

form. This band is the only halloysite reflection observed after the successive grindings (Fig. 1), and for this reason it has been impossible to choose another.

In Figs. 2–4, by means of the electron microscope, the successive destruction of the halloysite crystals during the grinding is observed.

The alteration of the halloysite has been realized under room conditions, treating 0.2 g of halloysite with 0.2 g of acid in 4 ml of water (molar relation $A1/EDTA = 2.27$ and $A1/oxalic = 0.70$) during time periods from 5 to 90 days for each one of the acids and different particle sizes mentioned beforehand.

The nature of the products resulting from the alteration of the halloysite has been studied by X-ray diffraction (powder method) and the morphologic changes have been followed by electron microscopy.

For the X-ray diffraction evaluation of the quantity of amorphous material formed during the grinding of the halloysite, and for the percentage calculation of neoformed kaolinite (in the resulting products of the alteration), potassium chloride at 50 per cent has been used as an internal standard. Previously, calibration curves were made from binary mixtures of potassium chloride with Eureka halloysite and

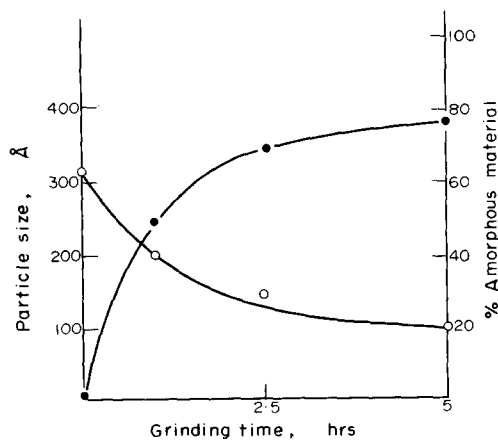


Fig. 5. Diminution of the halloysite particle size and formation of amorphous material in function of grinding time.

standard kaolinite (API No. 1) using the reflections 3.15 Å of potassium chloride, 4.43 and 3.60 Å of halloysite, and 7.15 and 3.57 Å of kaolinite.

In Fig. 5, the diminution of the halloysite particle size is shown, together with the simultaneous growth of amorphous material, as a function of the grinding time.

RESULTS

Alteration with oxalic acid

All the different sizes of the halloysite particle altered with oxalic acid have undergone a recrystallization that culminates around 20–30 days of treatment; after which time it gradually shrinks or returns to the initial percentage, in agreement with the increase of time of halloysite–oxalic contact. The recrystallization is more significant the smaller the size of the treated halloysite particles.

Alteration with EDTA

Natural halloysite (halloysite A). During the first days of acid treatment, a sudden destruction of the halloysite is observed (Fig. 6). After 5 days the destruction continues, although with a much slower reaction speed. At the end of 60 days of treatment, no new crystalline materials have appeared. The natural halloysite treated with EDTA has not modified appreciably its morphology (Fig. 7), except for the presence of some coarser tubes, approx. 4 or 5 times larger than the original ones, that appear to be the result of a recrystallization.

Halloysite ground for 1 hr (halloysite B). This fraction recrystallizes during the first 20 days (Fig. 6), self-destructing continuously. After about 50 days, the curve stabilizes itself. Simultaneously, and about day 40, the presence of kaolinite begins to be observed.

Through the electron microscope, large newly-formed tubes and flat particles are observed (Fig. 8).

Halloysite ground for 2.5 hr (halloysite C). The starting material undergoes an initial recrystallization (un-

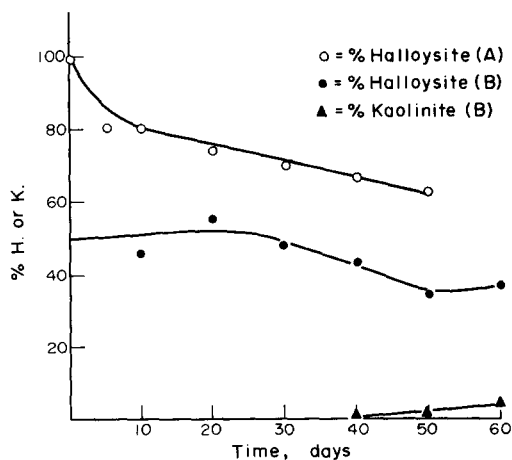


Fig. 6. Treatment of the A and B halloysite fractions with EDTA.

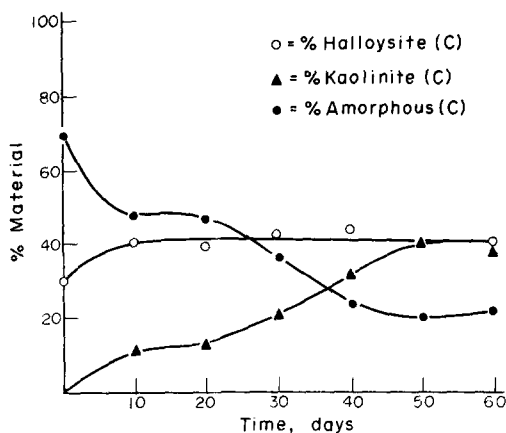


Fig. 9. Treatment of halloysite C with EDTA.

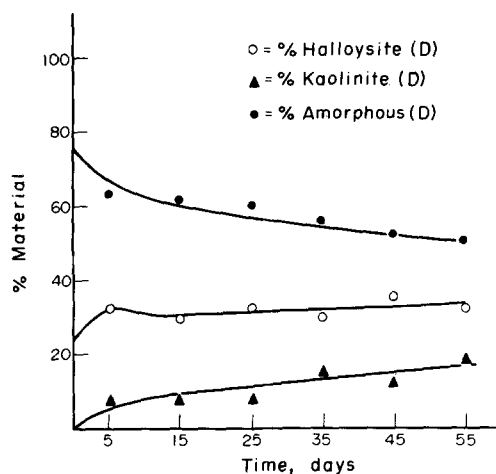


Fig. 11. Treatment of halloysite D with EDTA.

til day 10 of treatment). The percentage of halloysite then remains practically constant throughout the later treatment. The percentage of amorphous material, that drops sharply in the first 10 days (Fig. 9), stabilizes itself in the 10–20-day interval, and drops once again towards day 50 in which equilibrium is reached.

At the same time, and from the first few days, the appearance of kaolinite begins to be observed, and the kinetic curve of formation is symmetric with respect to that of the diminishing amorphous material. It must be specified that the two intervals of kaolinite growth coincide at that time with the two intervals of diminution of the percentage of amorphous material, which indicates an interdependence between the diminution of the latter and the formation of the kaolinite.

With the electron microscope, after 30 days of treatment, the presence of subrounded, flat and angular crystals is clearly observed. The tubular forms characteristic of halloysite hardly appear (Fig. 10).

Halloysite ground for 5 hr (halloysite D). The behaviour of halloysite D during the alteration is similar to that of fraction C (Fig. 11). The percentage of amorphous material decreases while that of kaolinite increases symmetrically with the previous curve.

During the first few days, a recrystallization of halloysite occurs, that morphologically shows itself as coarse tubes of variable length. On day 35, small-sized particles of kaolinites appear, coexisting with tubular halloysites and amorphous material (Fig. 12).

By day 90, the halloysitic material has practically

disappeared (Fig. 13) and small-sized crystals of kaolinite show up ($0.1\text{--}0.2\ \mu\text{m}$), sometimes subrounded and at other times of a good hexagonal morphology, together with amorphous material (Fig. 14).

DISCUSSION

Influence of the organic acids

The mechanism of the reaction has probably consisted of an attack by the acid on the 'amorphous' as well as crystallized halloysite, complexing aluminum and leaving silica in dissolution. The Al-organic acid complex formed, dissociates to the extent permitted by its constant of dissociation. In this particular case, the silica influences the concentration of aluminum in dissolution by the possibility of forming condensed phases of Si-O-Al type.

It is possible that the conditions of precipitation in homogenous solution for the synthesis of clay minerals at low temperature are those postulated by La Iglesia and Martin Vivaldi (1974). The Al-organic acid complex has served as a source of aluminum liberating it at a velocity suitable for the crystal growth rate. If the dissociation constant of the Al-organic acid compound is low, the liberation velocity of Al^{3+} will be high and therefore the product of the microconcentration of SiO_2 with that of Al^{3+} , in whatever point of the system, will exceed to the solubility product of the kaolinite or halloysite and will produce a silico-alumina gel, since a large quan-

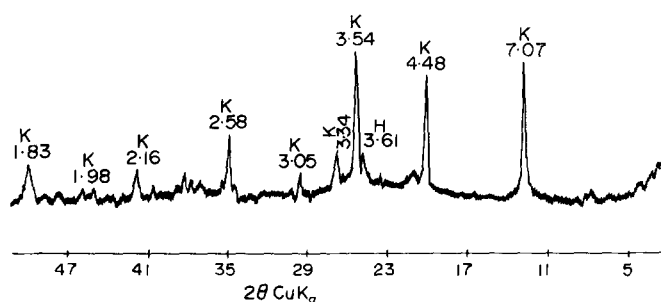


Fig. 13. X-ray diffraction pattern of halloysite D treated with EDTA during 90 days.

tity of crystalline nuclei appear, and the dissolution becomes poorer in aluminum and silica. Probably this is the process occurring in the alteration with oxalic acid. Under these conditions, the difference between the free energy of formation of kaolinite and halloysite is in favor of a partial crystallization of halloysite.

On the contrary, the EDTA-Al complex with a larger dissociation constant starts a lower Al^{3+} microconcentration, which permits the crystallization of kaolinite in these experimental conditions.

The speed of attack of the halloysitic material depends on the pK of every acid considered. The oxalic acid has a pK of 1.19 while the EDTA has a pK of 2.02, for which one can expect a much more intense attack than the first, besides bearing in mind that the oxalic acid is much more soluble than the EDTA. Both factors condition a rapid formation of the Al-oxalic complex that would give, as a final consequence, an increase of the microconcentration of Al^{3+} and a tendency towards the formation of an amorphous silico-aluminic phase.

Experiments similar to these have been carried out by Dennfeld *et al.* (1970), crystallizing kaolinite at hydrothermal temperature, starting with ground gibbsite and amorphous silica, and using various organic acids as catalyzers. These authors conclude that the Al-organic acid complex with a smaller dissociation constant are those which favor the crystallization of kaolinite. The disagreement with the present results can be due to the stability variation of the compounds in the temperature function and to that of the pK of the acids (hydrothermal conditions for Dennfeld and room conditions in our experiments). Kittrick (1970), on obtaining kaolinite at room temperature starting with montmorillonite in an equilibrium solution for 3-4 years, with acid dissolutions, demonstrates that only the dissolutions with concentrations of SiO_2 and Al^{3+} supersaturated with respect to the kaolinite, crystallize as kaolinite. In the present case, this supersaturation is guaranteed in all the samples of ground halloysite.

Influence of particle size

The attack on a solid phase depends on its exposed area. Therefore, the finer the sample is, the greater the attack velocity will be. On the other hand, in the grinding, small 'amorphous' crystals rich in active places are obtained and these serve as nucleant agents in the crystallization. The recrystallization of the halloysite in the first days of treatment can be explained in this manner (see Figs. 6, 7, 10 and 12). This action confirms precisely that the A halloysite (Fig. 7), an unground sample, does not recrystallize and also dissolves itself.

In the process of alteration with EDTA it has been proved that the fraction which produces the most kaolinite is C and not the fraction with the smallest size (D fraction), as it would be expected. This possible anomaly can be explained because fraction D dissolves itself rapidly, obtaining a supersaturation with respect to the kaolinite and precipitating amorphous phases.

In the case of fraction B, the solubility of the halloysite and the crystallization rate of the kaolinite are so small that their growth is not appreciable before day 30.

GEOLOGICAL INTERPRETATION

In the transformation sequences observed or suggested by the different authors cited in the introduction, the metahalloysite-ordered kaolinite step is effectuated through disordered kaolinite, by means of an intense weathering action, and enlarging the mid-size crystals formed.

In these experiments well-formed kaolinite has been obtained, although small in size and of irregular morphology. The halloysite-ordered kaolinite step does not necessarily proceed through disordered kaolinite.

Halloysite can become amorphous and will liberate aluminum under intense weathering action. This aluminum may or may not be complexed according to characteristics of the complexing substances. If Al^{3+} is complexed earlier, under the influence of silica in solution, kaolinite will be crystallized. In nature, the halloysite-ordered kaolinite transformation will take place when it is subjected to an intense weathering action in the presence of Al-complexes and with partial washing of the silica. The sequence will be:

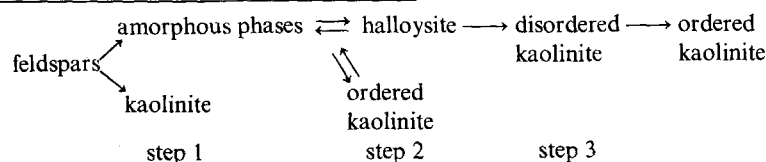
halloysite → amorphous phase → ordered kaolinite.

If the aluminum is not complexed, it will form an amorphous phase at other levels and in the presence of silica. This amorphous phase can be transformed into halloysite or kaolinite by an ageing process. This last transformation is increased if a new washing of silica occurs, and then gibbsite can be formed also.

Feldspars can be transformed into kaolinite or into amorphous silico-aluminic phases, by hydrolysis (step 1), depending on the weathering conditions. The amorphous phase can become kaolinite or halloysite (step 2), according to its crystalline predisposition and nucleation influence.

In the last case, by ageing (step 3) the structure can be reordered, first to disordered and then to ordered kaolinite; by an intense washing it can become amorphous and if the conditions of step 2 are repeated, ordered kaolinite will be formed.

The various sequences suggested can be summarized graphically as follows:



The type of kaolinite synthesized is similar to that of flint clay type kaolins. Therefore in the genetic processes of flint clay kaolins (normally related to the levels of organic matter) similar conditions to those of these experiments, although with different complexes, may have occurred.

REFERENCES

- Brindley, G. W. and Robinson, K. (1948) Structure of meta halloysite: *Miner. Mag.* **28**, 393–406.
- Chen, P. Y. (1969) Occurrence and genesis of kaolin minerals from Taiwan (I). Kaolinite, halloysite and allophane: *Proc. Geol. Soc. China* **12**, 30–48.
- Dennfeld, F., Siffert, B. and Wey, R. (1970) Etude de l'influence des complexants de l'aluminium et du broyage des hydroxides d'aluminium sur la formation hydrothermale de la kaolinite: *Bull. Groupe Franç. Argiles* **XXII**, 179–190.
- Fieldes, M. (1955) Clay mineralogy of New Zealand soils—II: Allophane and related mineral colloids: *N.Z. J. Sci. Technol.* **37**, 336–350.
- Galan, E. and Martin Pozas, J. M. (1971) Mineralogía de los caolines de La Guardia y El Rosal (Pontevedra, España): *Est. Geol.* **27**, 75–80.
- Galan, E. (1972) Caolines españoles. Geología, mineralogía y genesis. Thesis. Sciences Faculty, University of Madrid, Spain.
- Galan, E. and Martin Vivaldi, J. L. (1973) Caolines españoles. Geología, mineralogía y genesis—III: Clasificación de los depósitos de caolines españoles según su ambiente genético: *Bol. Soc. Esp. Ceram. y Vidrio.* **12** (6), 333–340.
- Hem, J. D., Roberson, C. E., Lind, C. J. and Polzer, W. L. (1973) Chemical interactions of aluminum with aqueous silica at 25°C: *Geol. Survey Water-supply Paper*, 1827-E, p. 57.
- Keller, W. D. (1964) Processes of origin and alteration of clay minerals. *Soil Clay Mineralogy* (Edited by Rich and Kunze), pp. 3–75. The University of North Carolina Press, Durham, North Carolina.
- Kinoshita, K. and Muchi, M. (1954) Bauxitic clay derived from volcanic ash: *Kyushukozan-gakkai* **22**, 279–291.
- Klug, H. P. and Alexander, L. E. (1954) *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. Wiley, New York.
- La Iglesia, A. and Martin Vivaldi, J. L. (1974) Synthesis of kaolinite by homogeneous precipitation at room temperature (I). Against anionic resins in (OH) form: *2nd Meeting of the European Clay Groups, Strasbourg*. In press.
- Martin Pozas, J. M., Galan, E. and Martin Vivaldi, J. L. (1971) Il giacimento di caolino di Jove (Lugo, España): *Atti. 1^o Congresso Naz. Grup. Ital. AIPEA*, 89–109.
- Ponder, A. and Keller, W. D. (1960) Geology, mineralogy and genesis of selected fire-clays from Latah Country, Idaho, pp. 44–63: *Clays and Clay Min. 8th Conf.* Pergamon Press, Oxford.
- Sudo, T. and Takahashi, H. (1956) Shapes of halloysite particles in Japanese clays, pp. 67–79. *Clays and Clay Min. 4th Conf. Nat. Acad. Sci.* **456**, Washington.
- Tamura, T. and Jackson, M. L. (1953) Structural and energy relationships in the formation of iron and aluminium oxides, hydroxides and silicates: *Science* **117**, 381–383.