

THE BENTONITES OF CABO DE GATA (SOUTHEAST SPAIN) AND OF GUELAYA VOLCANIC PROVINCE (NORTH MOROCCO)*

by

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ABSTRACT

Volcanic activity was important in Spain during the second half of the Cenozoic Era. It was closely related to the late kinematic and subsequent periods of the Alpidic orogenic cycle. Manifestations of the volcanic activity are seen in several parts of the Iberian Peninsula, but the main ones were confined to a few rather individualized zones. Cabo de Gata, Cartagena, and Mazarrón show a strong similarity, as does the Guelaya volcanic province, Morocco. The rocks (rhyolites, dacites and andesites) are clearly calcalkaline and, in many places, strong contamination processes have been demonstrated. The eruptions were, at least in part, fissural and fill important fractures, mainly northeast-southwest. They occurred just after the more important folding in the Betic-Riffien orogen. In these regions bentonite has formed by alteration of volcanic material.

The most important deposits are in Sierra of Nijar and Gata (Almería, Spain) and in the Monte Tidinit (Morocco). The Cabo de Gata bentonites are composed mainly of calcic and calcosodic montmorillonites. Palygorskite has been found in some places.

The bentonite of the Monte Tidinit is mainly calcium montmorillonite but some samples contain cristobalite. In Monte Maazza there is also a sedimentary deposit, consisting of a complex mixture of endellite, halloysite, gibbsite, montmorillonite and alunite—probably of hydrothermal origin. Halloysite is the main component: it is accompanied by gibbsite in the bottom layers and by montmorillonite and alunite in the top ones.

The ground clay, after processing by cation exchange or acid activation, is used for several industrial products, such as soaps and detergents, cosmetics and pharmacy; but the main use is for drilling muds, foundry molds, and clarification of mineral and vegetable oils.

All the bentonites are amenable to acid activation but the natural mixture of halloysite and montmorillonite from Monte Maazza gave the best results in tests on lubricating oils at a laboratory scale.

Research still in progress on the rheology of suspensions of the Almería bentonite contaminated with electrolytes gave interesting results using several thinner and filter oss control agents.

MINERALOGY AND GENESIS OF THE DEPOSITS

The Volcanic Regions

The geographic configuration of Spain (Solé Sabaris, 1938, p.267) is due to the distribution of the following structural elements: The central plateau,

* Presented before the 10th Conference in the Symposium on Bentonites, and published by permission of the Director of the Estación Experimental del Zaidin.

with its mountainous rim; the depressions outside this plateau (Ebro, Guadalquivir) and the peripheral ranges. Among these are the Betic and Pyrenaic orogenic systems. Most hypotheses relating to the trend of these folds in the Iberian peninsula note their continuation to the north of Africa along the Riffien Atlas, after a deflection at the Strait of Gibraltar.

In relation to the late kinematic and subsequent periods of this Alpidic orogenic cycle, volcanic activity has been important in Spain during the second half of the Cenozoic Era. Manifestations of volcanic activity are seen in several parts of the Iberian Peninsula, but the main ones are confined to a few rather individualized zones. Cabo de Gata, Cartagena and Mazarrón are part of a single volcanic region which extends to the south through the Alboran isles to the Guelaya volcanic province. Parga Pondal (1935) names this region "zona orogénica bética"; it is shown as a hachured zone in Fig. 1, where some other volcanic regions in the peninsula can be seen.



FIGURE 1.—Volcanic regions in the Iberian peninsula (Parga Pondal, 1935).

The Volcanic Rocks

The Cenozoic volcanic rocks of these regions were first studied by Calderón (1882) and Ossan (1889; 1891a; 1891b) and more recently by Parga Pondal (1935), Burri and Parga Pondal (1948), Fuster and Ibarrola (1952), San Miguel, Almela and Fuster (1952), Fuster and de Pedro (1953), and Fuster (1956a; 1956b; 1957).

The volcanic region of Cabo de Gata is composed (Fig. 2) of three almost parallel ranges trending northeast-southwest: the easternmost range (Sierra del Cabo y Mesa de Roldan), a middle range (La Serrata), and the westernmost one having centers of eruption in four zones (Hoyazo, Vera, Mazarrón and Cartagena). As the bentonites of this region are found only in the Serrata and recently at several points in Sierra del Cabo, in its northern part, we shall refer only to these rocks. The dominant volcanic rock of the Serrata (Ossan,

1889) is a hornblende dacite. Smaller amounts of a pyroxenic andesite locally intrude the dacite mass. Abundant volcanic tuff, perlite and, pumice overlie the dacite. In Sierra del Cabo on the contrary, pyroxene andesites are the most common rocks.

In a recent study of the volcanic rocks of the Serrata, Fuster (personal communication, 1961) found perlites in welded lavas, amphibolic dacites and pyroxenic andesites. The present author has verified the presence of these types of rocks, at least in the regions where the clay deposits are located.

According to the observations of Ossan, the flow structure or amygdaloid character typical of young volcanic products is absent. He thinks the volcanic rock originated as a great flow that later was eroded, giving birth to dome-shaped hills. However, we have found fragments of perlites with typical amygdules, from 2 to 4 cm in length.

In regard to the relative age it seems that the oldest rocks (Ossan, 1889) are the hornblendic and micaceous andesites and the hornblendic dacites (pre-Pliocene and subaerial), and that the pyroxenic andesites, liparite, and pumiceous tuff are younger (Pliocene). Fuster (personal communication, 1961) thinks the oldest is the perlitic welded tuff.

In the Guelaya province are two volcanic complexes (Fuster, 1956a;

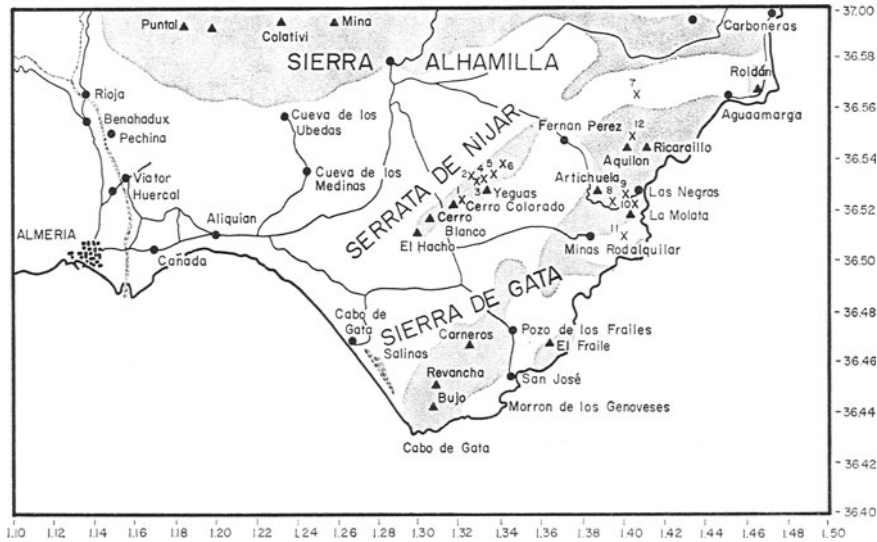


FIGURE 2.—The volcanic region of Cabo de Gata, showing location of bentonites and samples. (1) Archidona deposit; (2) Cortijo Blanco (test pit); (3) Pecho de los Cristos South (test pit); (4) Pecho de los Cristos deposit; (5) Pecho de los Cristos (North) deposit; (6) Palma del Muerto, exhausted deposit; (7) Huerta Grande (los Trancos) deposit; (8) Rambla de los Perez deposit; (9) Cerro del Aire (test pit); (10) Rambla del Cuervo (test pit); (11) Cortijo Colorado deposit; (12) Majada de las Vacas deposit.

1956b): (a) the Gurugu complex, with emission centers at the Gurugu and Tidinit, among others, and made up of an accumulation of basic and intermediate rocks of andesitic composition; and (b) the Tres Forcas complex, composed almost exclusively of acid rocks (dellenitic and rhyolitic) and even more acid pyroclastic products. Volumetrically unimportant basaltic flows are present locally.

The rocks of the Gurugu complex are potassium-rich andesites of vitreous porphyritic texture, with phenocrysts of plagioclase, biotite and pyroxene. In addition to these, Fuster mentions more vitreous and acidic types that approach the chemical composition of the dellenitic or rhyolitic lavas of Tres Forcas.

The age of the volcanic activity is cited as pre-Pliocene (Tres Forcas) and Pliocene (Gurugu and Tidinit). The basaltic flows must be younger—latest Pliocene or Quaternary.

The volcanic activity in each complex, then, became progressively more basic. From this fact and after careful study of the chemical composition of the rocks (Fuster, 1956b; 1957), it is deduced that the rocks did not originate from simple magmatic differentiation but from the strong sialic formation that is present in all evolving synclinal zones. The volcanic rocks in the Guelaya must represent, then, the production of palingenic acid magmas.

Although we have yet no detailed data for the Serrata and the south of Sierra del Cabo, we may recall that Fuster (1956a), from his researches on the north part of the latter, concludes that, as for the Guelaya, there are also contaminations. We think thus that in the series of andesite-rhyolites accompanying the Riffien-Betic folding we are dealing with late-orogenic phases, in the sense of Stille, with at some centers stages of subsequent and final basaltic volcanism.

The Bentonites

The Moroccan bentonite deposits are located in the Tidinit volcanic complex* and the Peninsular bentonites in the Serrata and Sierra de Gata. Deposits of bentonites near Oran have been studied recently by Sadrán, Millot and Bonifas (1955); they originated by alteration of rhyolite, and their mineralogical composition is montmorillonite plus kaolinite. The rhyolite was altered along fractures by later volcanic action.

The Tidinit deposit.—Figure 3 shows the location of the bentonite deposits of the Guelaya. They were fully described by Gutierrez Rios (1948) and Gutierrez Rios and González Garcia (1949).

In these earlier reports it was pointed out that the bentonites formed by alteration of the andesites. From a later and more careful chemical, optical and mineralogical study of that series of rocks and alteration products we conclude (Gutierrez Rios, Martín Vivaldi and Pino Vazquez, 1957; Martín Vivaldi and Pino Vazquez, 1956b) that the parent rock is a leucorhyodacite,

* Some small deposits have been cited also in Tres Forcas and at the west of Cabo Quilates. (A. Gallego Bermejo, personal communication, 1961).

similar to the more acid rocks cited by Fuster. The lateral gradation from the unaltered rock (sample 37) to the bentonite is illustrated in the analyses of Table 1.

The mineralogical formula for the bentonite (sample 33) is:

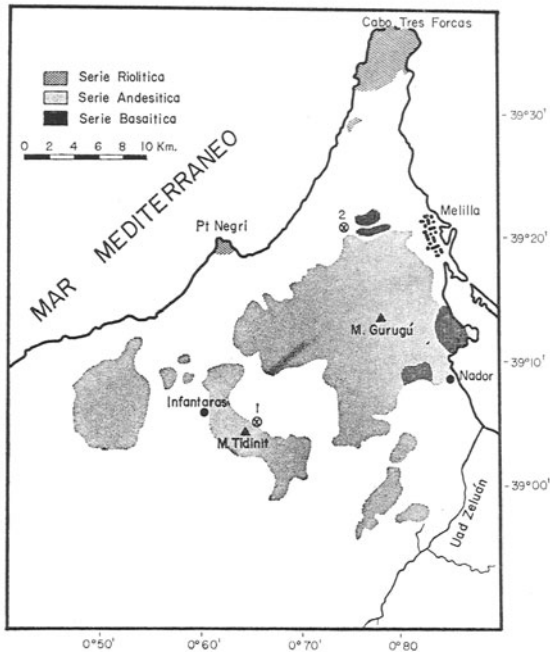
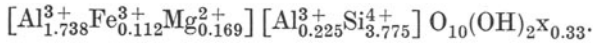


FIGURE 3.—Location of bentonite deposits of the Guelaya (North Morocco). (1) Tidinit deposit; (2) Maazza deposit.

X-ray diffraction maxima at 17 Å, DTA curves for the series, and the appearance of the bentonite in the electron microscopes are shown in Figs. 4 and 5 and Plate 1a. The following facts are obvious: (a) The rock is vitreous, acid, and rich in alkalis; (b) SiO_2 has been gradually removed and Mg added (see molar ratios, Table 1); (c) free SiO_2 is less mobile where the concentration of Mg is higher; and (d) samples richer in SiO_2 contain more cristobalite.

From these facts the genetic process must be the following (Martín Vivaldi and Pino Vazquez, 1956b): The feldspar (phenocrystal and normative) is altered with removal of alkalis and silica. Every two parts of glass produce one part of montmorillonite, in agreement with Correns and Engelhardt's (1938) results. Cristobalite is present only in those samples partly altered to montmorillonite and must be derived from the SiO_2 that is removed, and later coagulated in part by the Mg ions. As the amount of cristobalite is less in

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TABLE 1.—MOLAL RATIOS, pH OF SUSPENSIONS, FREE SiO₂, SiO₂/Al₂O₃ RATIO, AND MINERALOGICAL COMPOSITION DEDUCED FROM X-RAY DATA (TIDINIT DEPOSIT)

| | Sample | | | | | | |
|--|--------|------|------|-------|------|------|------|
| | 37 | 35 | 32 | 29 | 30 | 33 | 31 |
| SiO ₂ /Al ₂ O ₃ | 8.30 | 7.73 | 5.53 | 6.44 | 5.88 | 3.95 | 3.74 |
| Fe ₂ O ₃ /Al ₂ O ₃ | 0.03 | 0.04 | 0.07 | 0.07 | 0.07 | 0.06 | 0.04 |
| MgO/Al ₂ O ₃ | 0.00 | 0.05 | 0.22 | 0.30 | 0.20 | 0.17 | 0.21 |
| CaO/Al ₂ O ₃ | 0.34 | 0.23 | 0.14 | 0.09 | 0.09 | 0.08 | 0.09 |
| pH | — | 8.59 | 8.40 | 8.28 | 8.31 | 8.70 | 8.49 |
| Percent free SiO ₂ | — | 1.39 | 1.71 | 10.30 | 4.52 | 1.77 | 1.71 |
| SiO ₂ /Al ₂ O ₃ *— | 8.3 | 7.68 | 5.38 | 5.51 | 5.54 | 3.61 | 3.84 |
| Montmorillonite | — | 10 | 40 | 60 | 70 | 90 | 100 |
| Feldspar | 5 | 15 | 5 | 0 | 0 | — | — |
| glass | + | (?) | (?) | (?) | (?) | — | — |
| Cristobalite | — | — | 10 | 30 | 25 | 5 | — |

*Subtracting free silica

samples richer in montmorillonite it may be supposed to be the basis of the tetrahedral layer of the montmorillonite.

The Maazza deposit.—A bentonite deposit that may be genetically different is located at the foothill of Maazza Mountain. From the first studies (Gutierrez Rios, 1948; Gutierrez Rios and González Garcia, 1948) it was concluded that the main mineral was a member of the heidellite–montmorillonite isomorphous series. Later, from a more detailed study of the same samples, we concluded that the main components are endellite and halloysite (Martín Vivaldi and Girela Vilchez, 1958). Jeanette, Moniti6n and Ortelli (1958) arrived at similar conclusions. We have continued the study of these samples and a full report will be published elsewhere (Girela Vilchez, 1961).

Maazza Mountain, 7 km from Melilla and near Zoco al Had on the north side of the Gurugú Mountain, is on the rim of Tertiary sediments between Melilla and Tres Forcas. Figure 6 shows the stratigraphic section at the locality from which the group of samples was collected, after the description by Gutierrez Rios (1948). Limestone and sandstone layers, with fossils, are interbedded with the bentonite. Above it are red clays, calcareous marl, limestones, and a basaltic flow at the top. These sediments are shallow-water deposits of Neogene age, contemporaneous with the bentonites from Tidinit and Almería, and thus are related to the volcanism of the region.

The deposit is richer in alumina in the lower layers and more silicic in the upper ones. Chemical analyses of the samples are shown in Table 2.

Mineralogical analysis by several experimental techniques shows that the

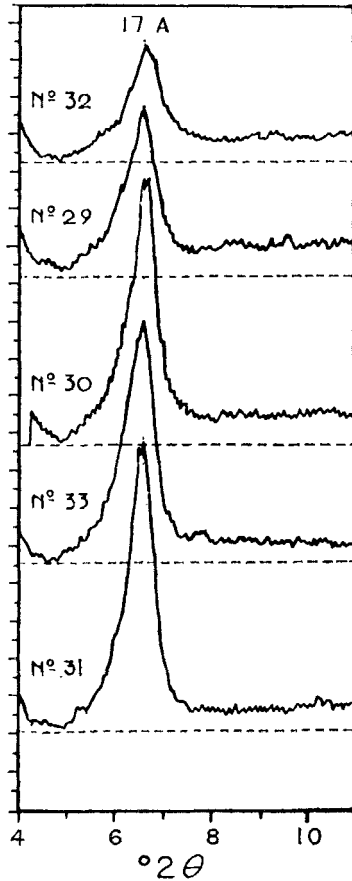


FIGURE 4.—X-ray diffraction maxima at 17 Å for the Tidinit samples (Gutierrez Ríos, Martín Vivaldi and del Pino, 1958).

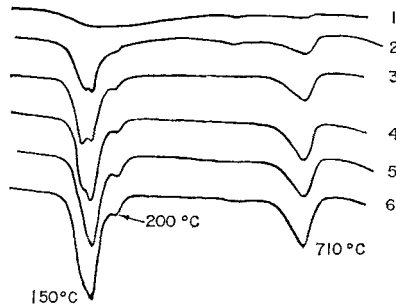


FIGURE 5.—Differential thermal curves for the Tidinit samples.

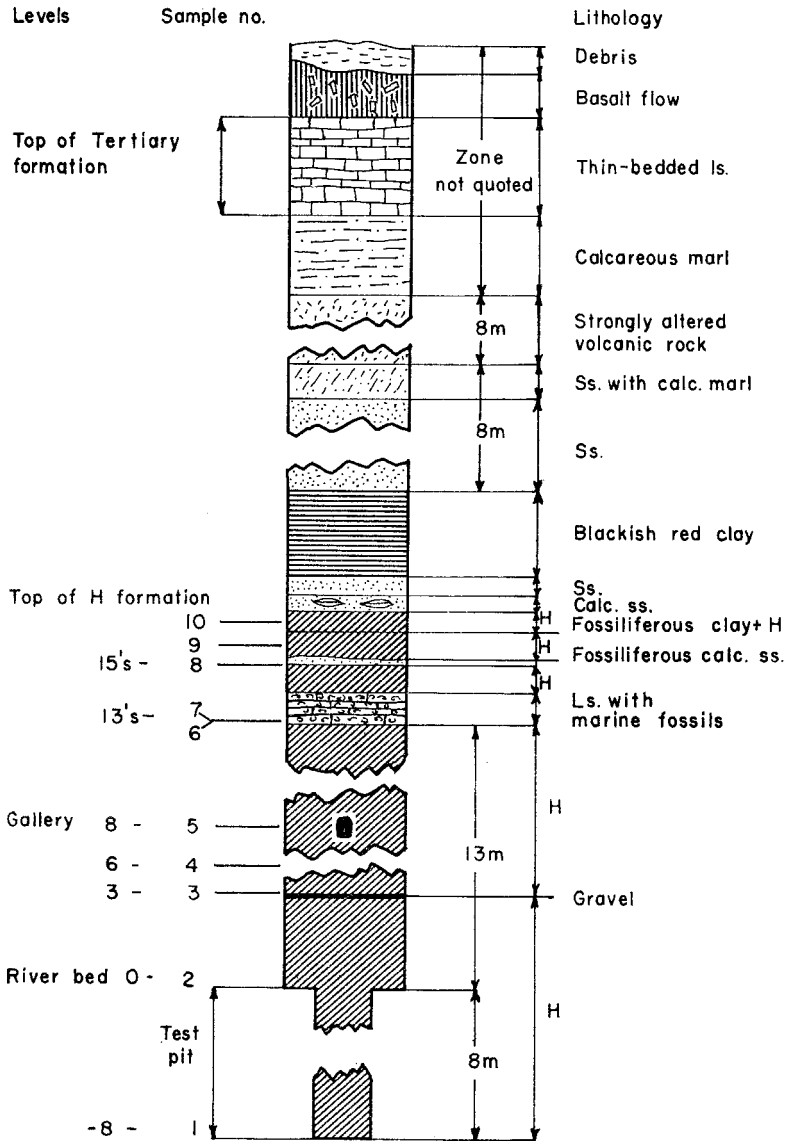


FIGURE 6.—Geologic sections of the halloysite deposits (H = halloysite) (Martín Vivaldi and Girela Vilchez, 1959).

TABLE 2.—CHEMICAL ANALYSES (MAAZZA DEPOSIT)

| | M-2 | M-3 | M-4 | M-5 | M-6 | M-7 | M-8 | M-9 | M-10 |
|--------------------------------|-------|--------|-------|--------|--------|-------|--------|-------|--------|
| SiO ₂ | 39.10 | 33.19 | 27.12 | 35.42 | 43.65 | 43.65 | 45.50 | 38.82 | 43.20 |
| Al ₂ O ₃ | 37.32 | 45.65 | 41.84 | 43.07 | 44.75 | 38.91 | 38.63 | 35.72 | 36.99 |
| TiO ₂ | 0.33 | 0.12 | — | — | 0.35 | 0.36 | 0.27 | — | — |
| Fe ₂ O ₃ | 2.48 | 1.51 | — | — | 3.00 | 1.43 | 0.70 | 1.76 | 0.91 |
| CaO | 1.60 | — | 1.37 | 0.90 | — | 2.48 | — | 0.22 | 0.86 |
| MgO | 3.34 | — | 1.08 | — | — | 1.90 | 1.65 | 1.90 | 2.77 |
| SO ₃ | | | | | | | | 6.95 | |
| Ign. Loss | 15.82 | 16.85 | 28.32 | 20.75 | 9.77 | 9.84 | 13.52 | 13.27 | 16.05 |
| Total | 99.99 | 100.33 | 99.73 | 100.13 | 101.52 | 98.57 | 100.52 | 98.64 | 100.78 |
| H ₂ O— | 3.83 | 3.78 | 3.36 | 3.37 | 4.90 | 5.51 | 6.47 | 8.18 | 8.66 |
| CO ₂ | 0.13 | 0.20 | 0.20 | 0.23 | 0.23 | 0.13 | 0.10 | 0.13 | 0.13 |

lower layers of the deposit are composed of halloysite and gibbsite, with some endellite and sparse alunite. The upper layers of the bentonitic sediments contain halloysite, endellite, a dioctahedral mineral of the montmorillonite group, and alunite. Allophane is present in all samples.

Plate 2 shows X-ray diffraction photographs for the samples, and Figs. 7, 8 and 9 their DTA and thermogravimetric curves. The existence of endellite and montmorillonite also was demonstrated with DTA using the methods of Sand and Bates (1953) (Fig. 10) and Sudo (1954) (Fig. 11). It was necessary to determine the cation exchange capacity with Ba as the results with ammonium were too high and variable, owing to retention of ammonium salts (Garrett and Walker, 1959; Wada, 1959; Thomas, 1960).

The amount of endellite also was estimated by retention of ethylene glycol. As a montmorillonite mineral is also present it was necessary to desorb samples after heating irreversibly at 150°C. But if halloysite is maintained under ethylene glycol for extended periods of time it swells as does the endellite. The electron micrographs (Plate 1) shows the typical morphology of the halloysite crystals.

Semiquantitative spectrochemical analysis indicated the presence of potassium in all samples from the upper layers of the deposit and its scarcity in the lower ones. This distribution must be related to the variation in chemical composition of successive volcanic emissions.

Quantitative determination of the minerals has been made from X-ray diffraction photographs using an internal standard; from the areas under the peaks of DTA curves previously calibrated with standard mixtures; from thermogravimetric curves and through retention of ethylene glycol (Girela Vilchez, 1961; Martín Vivaldi and Girela Vilchez, 1961). Figure 12 shows the mineralogical composition as deduced from the above determinations, but omitting the halloysite-endellite differentiation in view of the limitations imposed on its accuracy by the alunite accessory. It is difficult to postulate

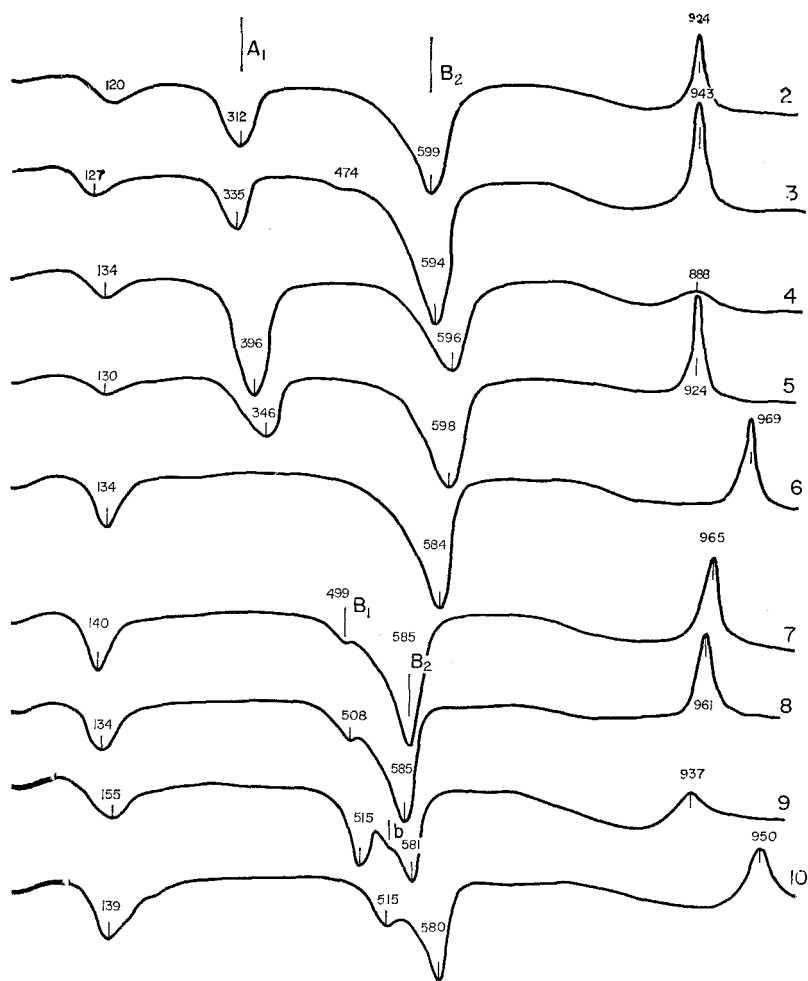


FIGURE 7.—Differential thermal curves for the samples from Maazza.

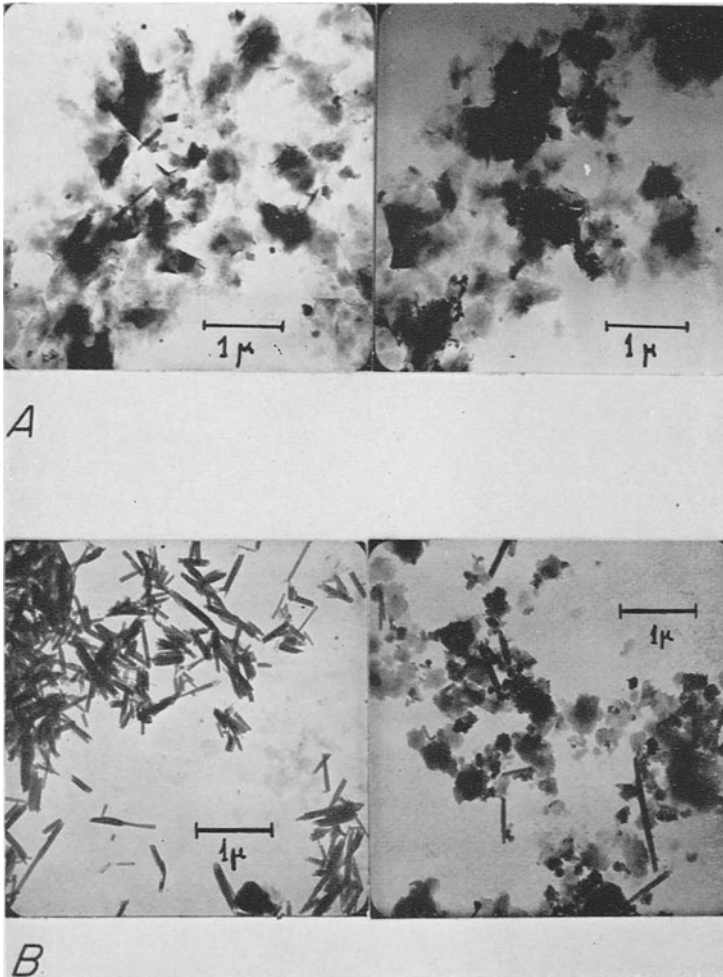


PLATE 1.—Electron micrographs. (A) Bentonite of Tidinit; fraction finer than 2μ . (B) Samples 1 and 2 from Maazza.

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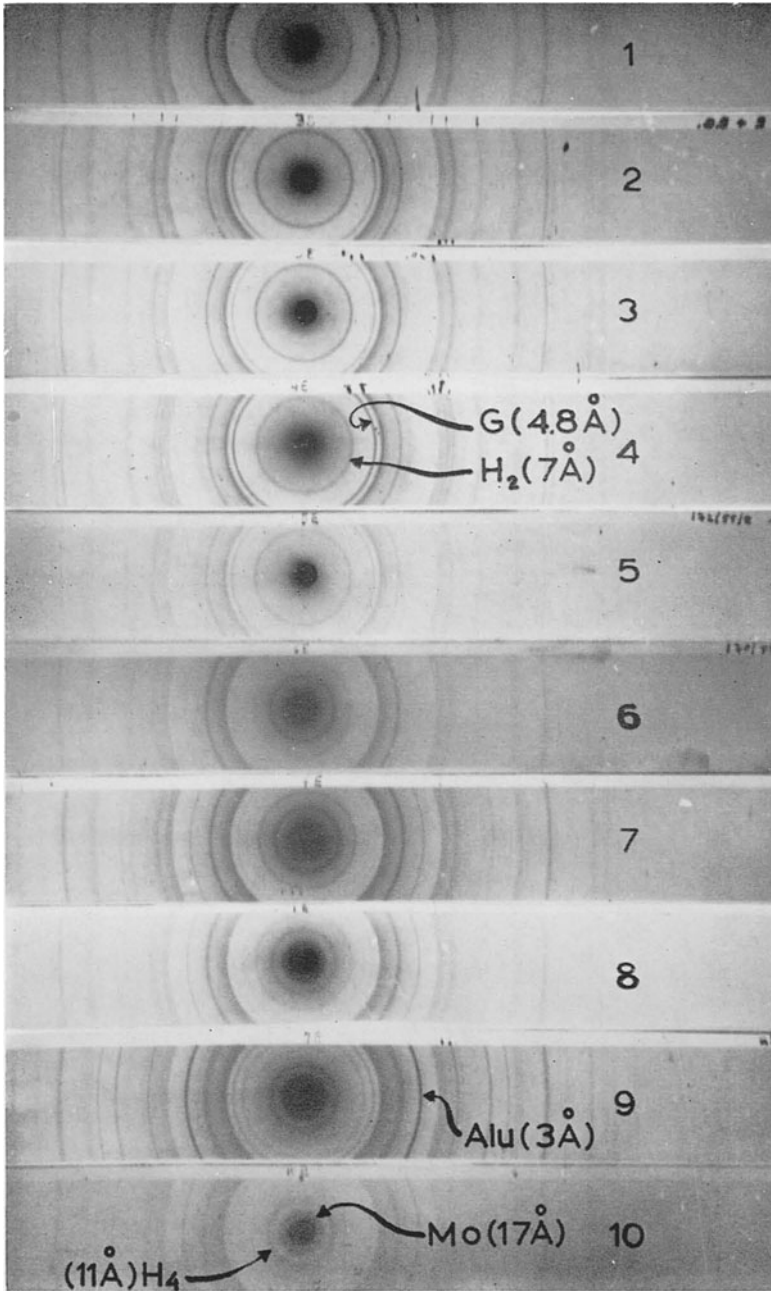


PLATE 2.—X-ray diffraction photographs for samples from Maazza.
 G = gibbsite; Alu = alunite; Mo = montmorillonite; H₂ = halloysite
 · 2H₂O; H₄ = halloysite · 4H₂O.



PLATE 3.—General view of the mining operation at Los Trancos, in the Sierra de Gata.

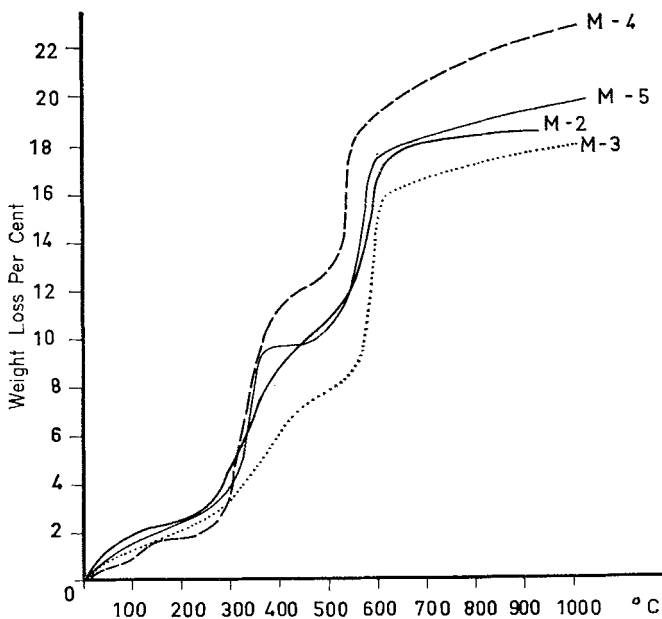


FIGURE 8.—Thermogravimetric curves for Maazza samples 2 to 5.

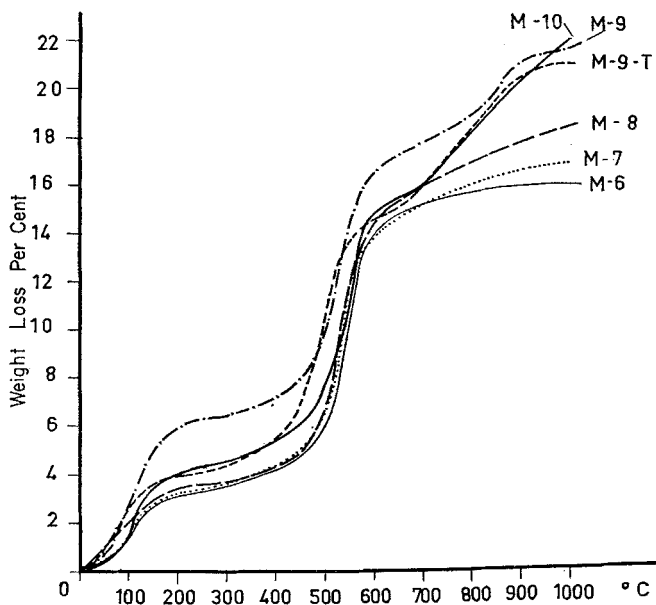


FIGURE 9.—Thermogravimetric curves for Maazza samples 6 to 10.

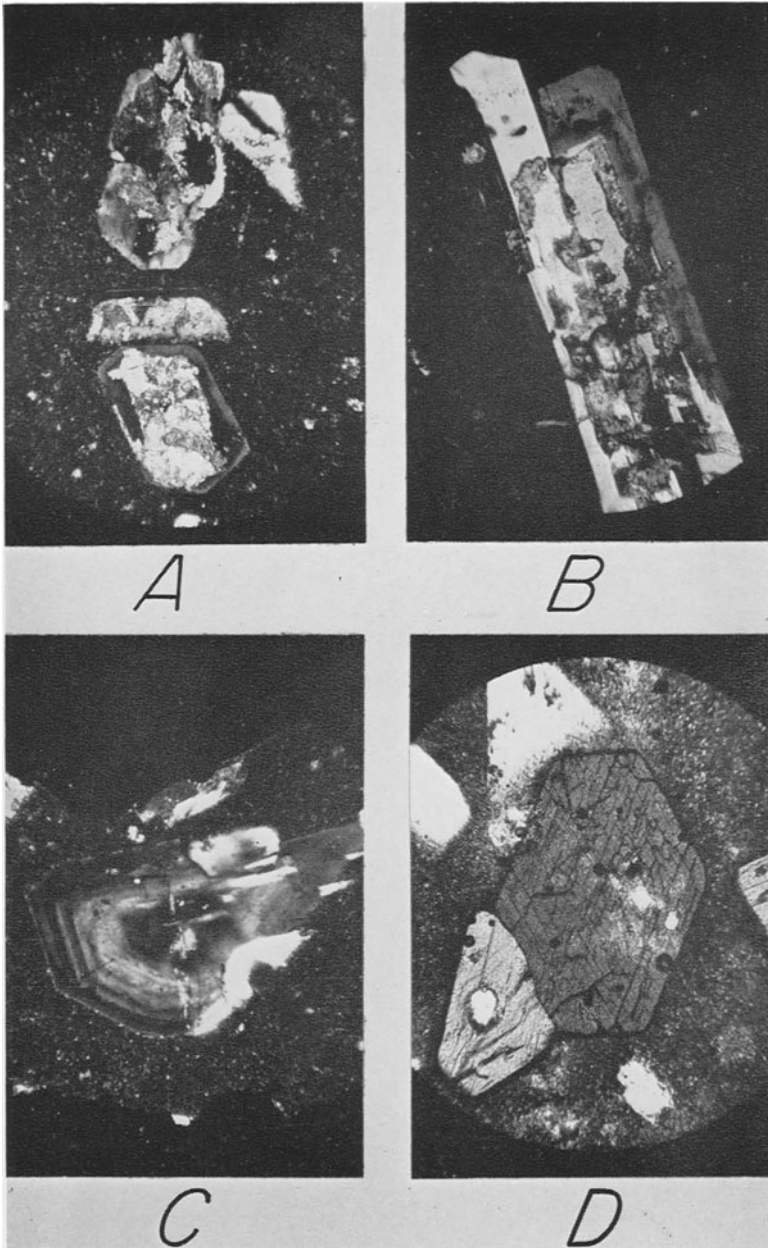


PLATE 4.—Photomicrographs of sample 120. (A and B) Plagioclase phenocryst in a vitreous matrix altered inside to calcium carbonate. (C) Zoned plagioclase phenocryst. (D) Amphibole phenocryst.
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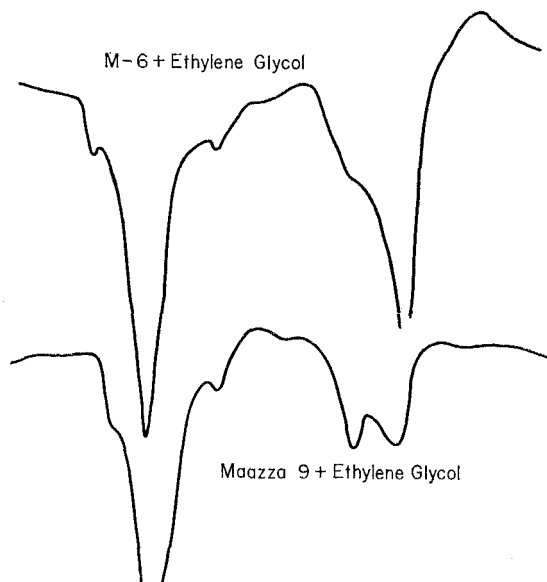


FIGURE 10.—Differential thermal curves for Maazza samples 6 and 9 treated with ethylene glycol.

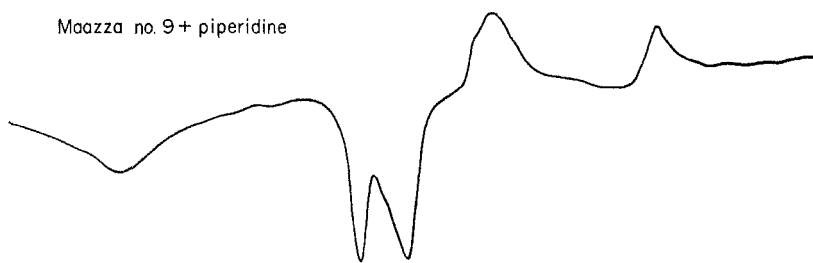


FIGURE 11.—Differential thermal curve for Maazza sample 9 treated with piperidine.

the genetic process for this deposit, but from analysis of the results compared with facts known from synthesis in the laboratory and the origin of similar deposits, we conclude that the clay minerals were formed by hydrothermal alteration of volcanic ash. The hydrothermal fluids removed abundant SiO_2 at moderate temperatures from the lower and presumably earlier-formed

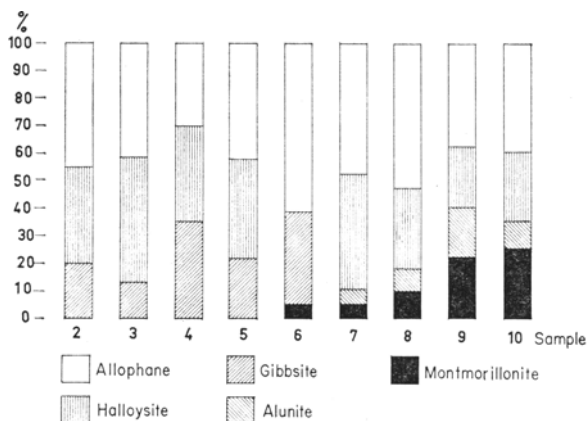


FIGURE 12.—Graph showing quantitative mineralogical composition of samples from Maazza.

parts of the deposit. It seems that the volcanic glass was altered first to allophane from which endellite crystallized; the excess of alumina produced gibbsite. The materials of the upper part must have been formed by the action of acid fluids rich in potassium, removing less SiO_2 and thus permitting formation of a montmorillonite mineral together with alunite.

Almería province deposits.—The bentonites from Almería are found almost exclusively in the amphibole dacite zones. However, our recent field observations, not yet confirmed by laboratory results, indicate that these bentonites are linked genetically with perlites and possibly with volcanic ash. We have observed (Majada de las Vacas) localities at which an altered dacite is clearly transformed into bentonite in which the bentonite preserves texture of the parent rock. This is true particularly at Los Trancos, and also in Sierra de Gata. But transitions of altered dacite to bentonite are not seen in the Serrata even though all the deposits occur where altered dacite is the dominant rock. The bentonite seems to be a subsequent fill, possibly an ash fall, which has since altered. Locally (Archidona), perlites in the bentonitic mass are digested and are transformed to red bentonite.

The descriptions that follow refer to samples from only two quarries: one in the Serrata (Palma del Muerto) and the other in Sierra de Gata (Los Trancos)*. A general view of the Los Trancos workings is shown in Plate 3.

* A full report including results on all the samples will be published elsewhere (Linares Gonzalez, 1961).

The series of samples from the Serrata (Palma del Muerto) include nos. 116₁-116₆. They were selected from a zone in which green and red bentonite (116₆) grades into a material that seems to be the altered parent rock. Sample 113a is a material of quite different character, located at the entrance to the gallery. No. 115 was selected from a point near 116₆, from an extensive green bentonitic mass that seemed very pure.

Figure 13 shows the DTA curves, and Table 3 shows the mineralogical composition deduced from the X-ray diffraction photographs. Table 4 refers to an oriented aggregate of < 2 μ e.s.d. for sample 113a, parallel and perpendicular to the X-ray beam, and shows that only in the perpendicular

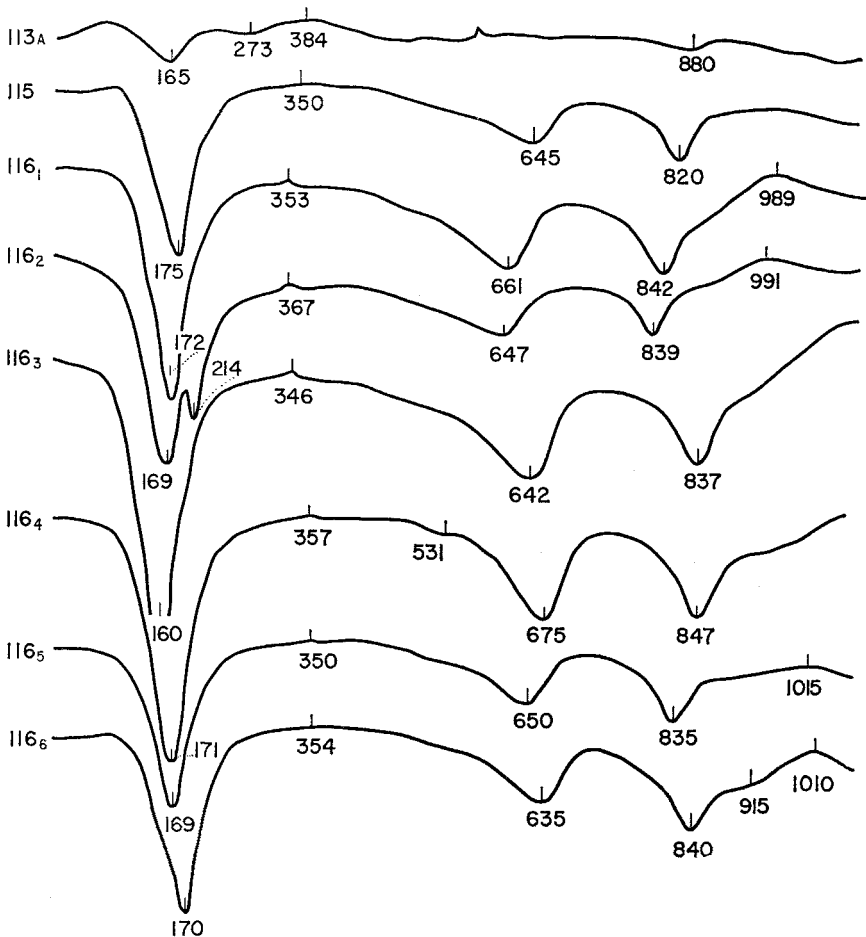


FIGURE 13.—Differential thermal curves for samples from Palma del Muerto (Serrata de Nijar, Almeria).

TABLE 3.—MINERALOGICAL COMPOSITION DEDUCED FROM X-RAY DIFFRACTION PHOTOGRAPHS (PALMA DEL MUERTO, SERRATA)

| Sample | Montmorillonite | Feldspar | Quartz | Palygorskite | Kaolinite |
|------------------|-----------------|----------|--------|--------------|-----------|
| 113a | + | ++++ | +++ | +++ | — |
| 116 ₁ | ++ | ++++ | — | — | + |
| 116 ₂ | ++ | +++ | — | — | + |
| 116 ₃ | +++ | ++ | — | — | — |
| 116 ₄ | ++++ | + | — | — | — |
| 116 ₅ | ++++ | + | — | — | — |
| 116 ₆ | +++++ | + | — | — | — |
| 115 | +++++ | + | + | — | — |

TABLE 4.—*d* SPACING AND INTENSITIES OBSERVED IN X-RAY DIFFRACTION PHOTOGRAPHS (SAMPLE 113a, < 2μ e.s.d.)

| 1* | | 2† | |
|----------|----------|----------|----------|
| <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> |
| 17.60 | s | | |
| 10.51 | s | 10.59 | s |
| 8.92 | vis | | |
| 6.50 | vis | 6.50 | vis |
| | | 5.43 | vis |
| 4.48 | vw | 4.48 | ms |
| 4.22 | w | 4.20 | s |
| 3.94 | vis | | |
| 3.79 | mw | 3.81 | w |
| | | 3.68 | w |
| 3.47 | vis | | |
| 3.34 | vis | | |
| | | 3.28 | s |
| 3.22 | vis | | |
| 2.99 | w | 2.95 | vw |
| 2.91 | vw | | |
| | | 2.58 | mw |
| | | 2.45 | mw |
| | | 2.17 | vw |
| | | 2.12 | vw |
| | | 1.79 | vw |
| | | 1.67 | vw |
| | | 1.56 | vw |
| | | 1.54 | vw |
| | | 1.50 | vw |

* Oriented aggregate parallel to X-ray beam.
 † Oriented aggregate normal to X-ray beam.

orientation can the palygorskite lines and *hk* band for montmorillonite be seen to be distinct from features which would have been afforded by any mica. Table 5 lists specific surface, and Table 6 chemical analyses of red and green montmorillonite, Table 5 also lists the quantitative estimation of montmorillonite for the series of samples, from X-ray diffraction photographs, using as a standard for mixtures the $<2\mu$ e.s.d. fraction of sample 115 and as internal standard a sepiolite from Vallecas.

TABLE 5.—SPECIFIC SURFACE, AND PERCENT OF MONTMORILLONITE DEDUCED FROM X-RAY DIFFRACTION PHOTOGRAPHS WITH INTERNAL STANDARD (PALMA DEL MUERTO, SERRATA)

| Sample | Total Area m ² /g | External Area m ² /g | Swelling Area m ² /g | % Montmorillonite |
|------------------|---------------------------------|------------------------------------|------------------------------------|----------------------|
| 116 ₁ | 624 | 98 | 526 | 55 |
| 116 ₂ | 550 | 36 | 514 | 36 |
| 116 ₃ | 400 | 43 | 357 | 82 |
| 116 ₄ | 660 | 44 | 616 | 83 |
| 116 ₅ | 775 | 129 | 746 | 93 |
| 116 ₆ | 852 | 23 | 829 | 96 |
| 115 | 804 | 33 | 771 | —* |

* See Table 3. No determination using internal standard was made.

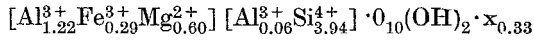
TABLE 6.—CHEMICAL ANALYSES OF MONTMORILLONITE FROM PALMA DEL MUERTO (SERRATA)

| | 115 (Green) | 114 (Red) |
|--------------------------------|----------------|--------------|
| SiO ₂ | 61.90 | 60.55 |
| Al ₂ O ₃ | 16.39 | 18.87 |
| Fe ₂ O ₃ | 6.32 | 6.88 |
| MgO | 4.58 | 5.30 |
| CaO | 0.65 | — |
| H ₂ O (—) | 9.54 | 8.88 |
| | 99.38 | 100.48 |

Selected samples from Sierra de Gata (Los Trancos) represent materials in a different stage of alteration to bentonite. Figure 14 shows the DTA curves; Table 7 the mineralogical composition from the X-ray data and the exchange capacity, and Plate 4 some aspects of the parent rock (a hornblende dacite) under the microscope.

The exchangeable cations in all these bentonites (Serrata and Sierra de Gata) are about 70 per cent Mg, with 20 per cent Ca and 10 per cent alkali and hydrogen cations. The mineralogical formulas of the montmorillonites are:

Los Trancos (Sierra de Gata); sample 124:



La Palma del Muerto (Serrata); sample 115:

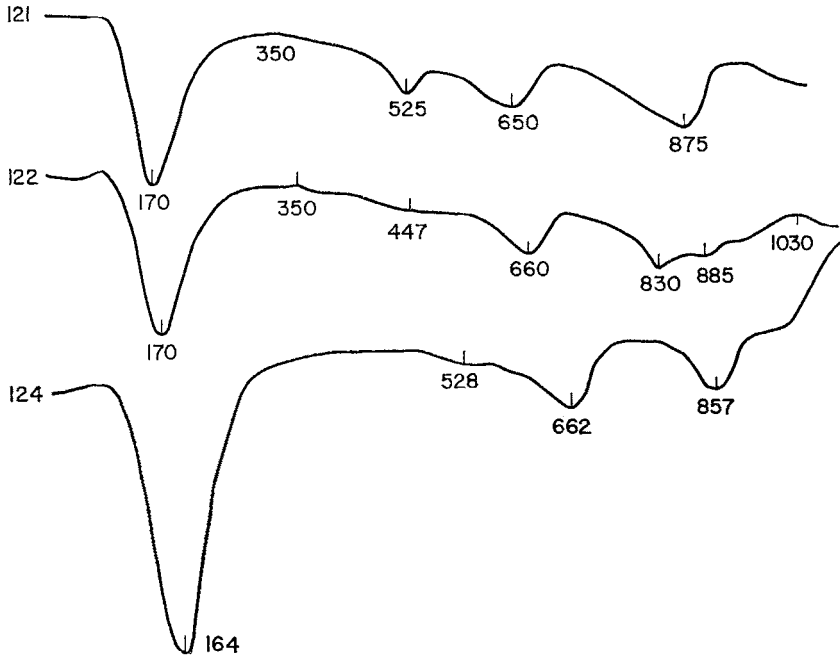
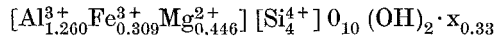


FIGURE 14.—Differential thermal curves for samples from Los Trancos (Sierra de Gata, Almeria).

TABLE 7.—MINERAL COMPOSITION DEDUCED FROM X-RAY DIFFRACTION PHOTOGRAPHS, AND CATION EXCHANGE CAPACITY (LOS TRANCOS, SIERRA DE GATA)

| | Sample | | | |
|-----------------|--------|------|------|------|
| | 120 | 121 | 122 | 124 |
| Montmorillonite | — | + | ++ | ++++ |
| Feldspar | ++++ | ++ | ++ | + |
| Quartz | ++ | + | + | — |
| Biotite | ++ | — | — | — |
| C.E.C (meq) | — | 76.6 | 91.6 | 97.8 |

Alteration of the volcanic rocks of Almería produces then a highly magnesian montmorillonite and, in several samples from the Serrata, attapulgite and kaolinite as well.

In the derivation of montmorillonite from its parent rock we note the removal of SiO_2 as well as addition of Mg. A semiquantitative spectrographic analysis of nearly fresh dacite, some altered dacites, and bentonite from Majada de las Vacas clearly shows an increase in Mg and a decrease in K, Rb, Cs, in passing from the unaltered rock to the bentonites. As is shown, this supply of Mg is as characteristic here as it is in the bentonites from Tidinit.

In the earliest research on these bentonites (González García and Martín Vivaldi, 1949; Martín Vivaldi and González García, 1951), we frequently saw a fibrous mineral in the electron microscope. We later concluded that it was palygorskite and that it commonly is associated with the bentonites of the Serrata. But in the deposits of Sierra de Gata (Los Trancos) a pinkish material that fills cracks in the bentonitic mass shows a fibrous morphology and gives higher spacing in the X-ray diffraction photograph (*ca.* 11 Å) than palygorskite. We assumed it to be a member of the sepiolite-palygorskite group (Martín Vivaldi, Cano Ruiz and Fontboté, 1956) but a more detailed study has led us to the conclusion that it probably is an intergrowth of sepiolite and palygorskite (Martín Vivaldi and Linares González, 1962).

The supply of Mg is higher in Almería than in Tidinit. This fact and a less silicic parent rock account for (a) the fact that all silica has become part of silicates, leaving a very small amount that is extractable with Na_2CO_3 (less than 2 per cent) and no cristobalite; and (b) the formation of magnesium-rich minerals of the sepiolite-palygorskite group.

Genetic Conclusions

We hope to get more conclusive experimental evidence but we may conclude that both volcanic regions—the southeast of Spain and the Guelaya province—not only are genetically related to the Alpidic orogeny, but also show a clear parallelism in type and age of volcanism, types of volcanic rocks, and contaminants. Further we hope to demonstrate close similarity in the mode of alteration of the rocks and in genesis of bentonite.

In fact, these bentonites have been found in the Guelaya and in Almería as alteration products from the vitreous and acidic rocks of the rhyolite-dacite series, where the andesites in both zones are only slightly altered. There, a supply of Mg to and removal of SiO_2 from volcanic vitreous calcalkalic acidic rocks—with intermediate formation of cristobalite in some cases—seems to be the general outline in the formation of the bentonites. The affinity between both formations—Peninsular and Moroccan—is even closer, in the sense that later, more acidic hydrothermal activity has produced kaolin and jarosite locally in the Sierra de Gata and endellite and alunite in Maazza.

Despite this uniformity, the variety of volcanic rocks, their processes of

contamination, and the variety of alteration products show the complexity of the volcanism associated with the late orogenic phase of the Alpidic folding in these regions.

PHYSICO-CHEMICAL STUDIES

Much physico-chemical research carried out in our laboratory on these bentonites has been summarized at these conferences (Albareda, 1956). To these we may add the study of the action of diazomethane on montmorillonite (Martín Vivaldi and Hendricks, 1952; Martín Vivaldi and Pino Vazquez, 1956a; Martín Vivaldi, Pino Vazquez and Cano Ruiz, 1956), the study of the thermal decomposition of NH_4 montmorillonite (Martín Vivaldi, Girela, Hernaiz and Rodriguez Gallego, 1959) the behavior of montmorillonite when treated with different exchange cations at various temperatures (Martín Vivaldi, MacEwan and Rodriguez Gallego, 1957) and the study of organic complexes of montmorillonite by DTA curves in normal and controlled atmospheres (Martín Vivaldi, Girela Vilchez, Rodriguez Gallego and Fenoll Hach-Alí, 1961).

TECHNICAL APPLICATIONS

Table 8 summarizes production and uses of the Almeria bentonites as reported by Minas de Gadar S.A. (Gallego, personal communication, 1961).

The bentonites from Sierra de Gata are activated by acid treatment and sold as "Tierras decolorantes" for use in decolorizing vegetable and mineral oils. Some are simply ground and screened to several standard sizes for use in percolation processes and for treating gasoline in the vapor phase.

The bentonites from the Serrata were found to be poorest for acid activation at an industrial scale. After conversion to sodium bentonites through a process of cation exchange, they are used as drilling muds, as bonds for foundry molds, and in soaps and cosmetics.

Our laboratory experiments (Gutierrez Rios and Lopez González, 1952a; 1952b; 1952c) have shown that all the bentonites described in the present paper are amendable to acid activation, but the mixture of endellite and montmorillonite from Maazza gave the best results when tested on a waste lubricating oil. We are now working with a standardized testing procedure for percolation and contact, using as standards a crude petroleum and a worn out lubricating oil (Martín Vivaldi, Hernaiz and Huertas, 1960). We have begun a study of the rheology of bentonite suspensions, mainly in the presence of saline contaminants. Up to the present we have tried only a filterloss control agent, a carboxymethylcellulose (here designated as E); and a thinner, an extract of humic acid (here designated as A).*

* A full record, including research using quebracho, pines ross, lignosulfonates, several carboxymethylcelluloses and pregelatinized starch, will be published elsewhere (Linares González, 1961).

TABLE 8.—PRODUCTION, SALES AND USES OF "BENTONITAS" AND "TIERRAS DECOLORANTES", MINAS DE GADOR S.A., ALMERÍA (GALLEGO, personal communication, 1961)

Production in tons

| Product | 1958 | 1959 | 1960 |
|------------------------|-------|-------|-------|
| Sodium bentonite | 2.951 | 3.689 | 4.431 |
| Calcium bentonite | 1.711 | 1.859 | 1.606 |
| "Tierras decolorantes" | 2.967 | 3.468 | 4.092 |
| Tierras granuladas | 40 | — | — |

Sales in per cent (Based on 1958 production)

| Uses | % |
|----------------------------------|------|
| Mineral oils | 16.5 |
| Edible oils | 24.0 |
| Gasoline in vapor phase | 0.5 |
| Drilling muds for oil wells | 14.0 |
| Drilling muds for water wells | 2.5 |
| Foundry molds | 40.5 |
| Conglomerate coals | 1.3 |
| Soaps, beer, wine and other uses | 0.7 |

As standard bentonite we used Gadorgel (almost sodic) as a 6 per cent suspension in water, aged 24 hr. Sodium chloride was used at four concentrations from 0.3 to 30 per cent.

The following cases were studied:

1. Bentonite suspension untreated.
2. Bentonite + NaCl at four concentrations of NaCl.
3. Bentonite + E for three concentrations of E.
4. Bentonite + E + NaCl. The four NaCl concentrations for each B + E.
5. Bentonite + A for the two different concentrations of A.
6. Bentonite + A + NaCl. The four NaCl concentrations for each B + A.

Table 9 shows the properties of the bentonite suspension without any additive; Fig. 15 shows the effect of sodic salinity on bentonite suspensions. Note that a low salinity concentration (about 1 per cent) gives a maximum on the viscosity curve typical of contaminated muds, but no other maximum is observed even up to 30 per cent salinity, as others (Rogers, 1953, p.299; Bergman and Fisher, 1950) have shown. The viscosity, then, is not seriously affected by medium or high concentration of salt, but the water loss is strongly affected and the thixotropy becomes very low.

TABLE 9.—RHEOLOGICAL AND OTHER PROPERTIES OF "GADORGEL"

| Property | 1 | 2 |
|-------------------------------------|-------|----|
| Viscosity (600 rpm) cp; fresh susp. | 18.5 | — |
| Viscosity (600 rpm) cp; aged susp. | 28 | 18 |
| Viscosity at 80°C, cp | 22 | — |
| Initial gel, g | 25 | 15 |
| 10 min gel, g | 60 | 45 |
| Thixotropy, g | 35 | 30 |
| Water loss (ml) | 17.7 | 16 |
| Filter cake, mm | 1.2 | — |
| Yield bbl/Tm. | 119.5 | — |
| pH | 7.0 | — |

1. Reported by "Minas de Gador"; Fresh 6 per cent aqueous suspension.
2. Six per cent aqueous suspension, aged 24 hr.

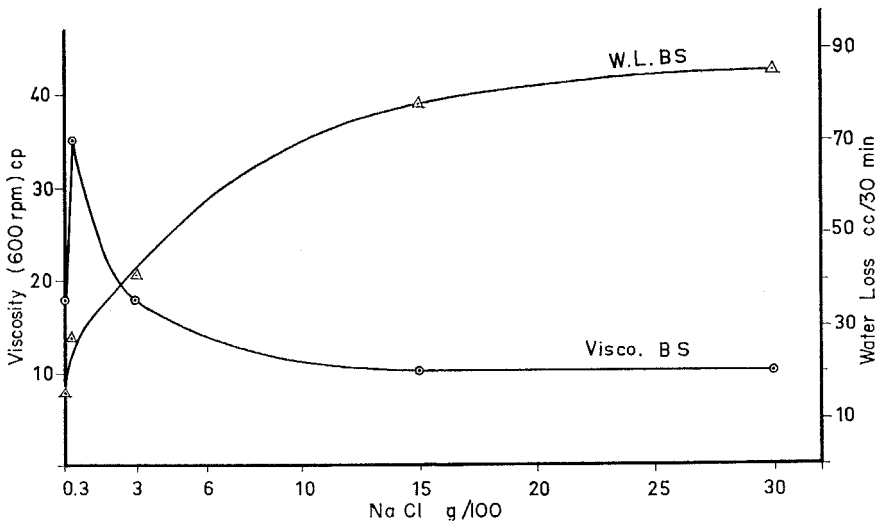


FIGURE 15.—Effect of NaCl on 6 per cent Gadorgel suspensions.

Figures 16, 17, 18 and 19 show the effects of A and E, independently, on the bentonite suspensions, without saline contamination. The water loss, viscosity and thixotropy are affected in the expected way, the thixotropic behavior of A being more satisfactory from a technical point of view. Figures 20–25 show the effect of the salinity on both prepared muds (bentonite + A, and bentonite + E).

The *water loss* is corrected as much by the water loss control agent (E) as by the thinner (A), at least up to medium salt concentration and using the appropriate concentrations for A and E.

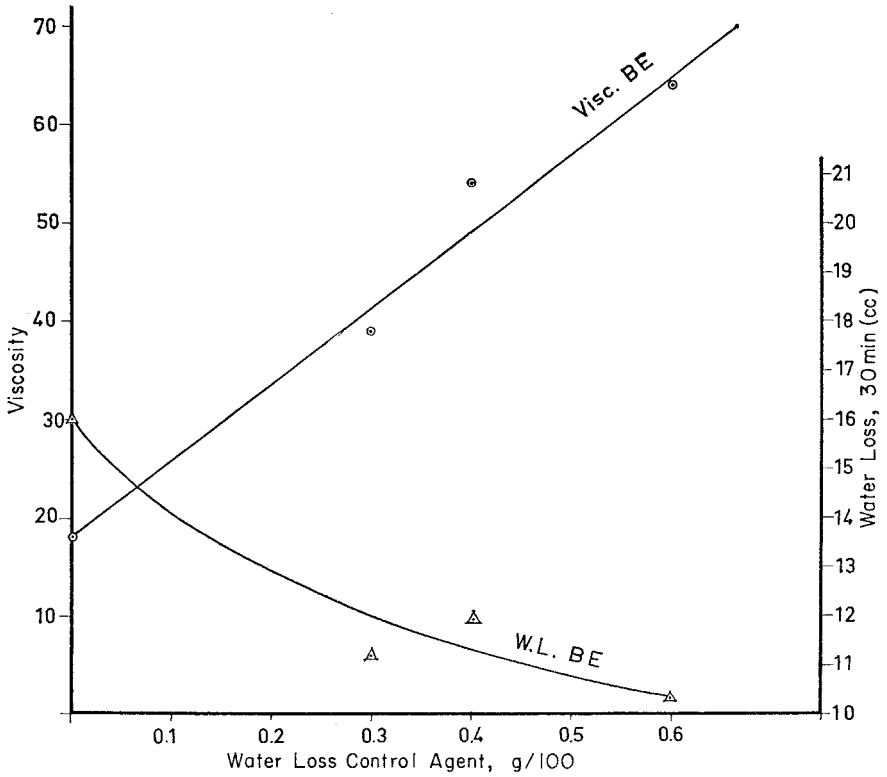


FIGURE 16.—Effect of water loss control agent (E) on Gadorgel suspensions.

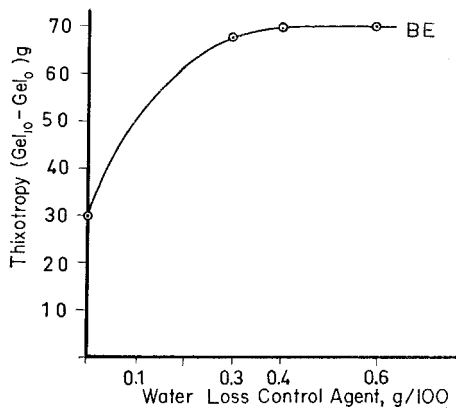


FIGURE 17.—Effect of E on thixotropy of Gadorgel suspensions.

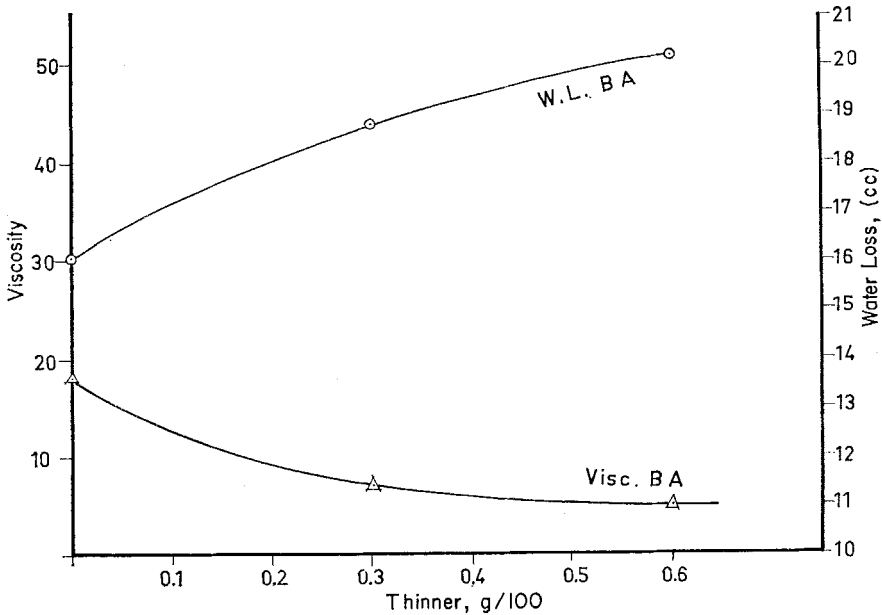


FIGURE 18.—Effect of thinner (A) on Gadorgel suspensions.

The *viscosity* is preserved with E within reasonable values if used at medium concentration. With A, results are good for both tested concentrations.

The *thixotropic* behavior of the mud is maintained within correct values if we select the proper concentration for E.

In resumé: Suspensions of Gadorgel up to saline concentration of 6 per cent have the right characteristics of a water based drilling mud, if there is no saline contamination.

Addition of the water loss agent prior to saline contamination is not recommended because, although water loss is improved, viscosity and thixotropy are worsened; but it can be used in saline water up to almost 6 per cent saline concentration.

The same is true for the thinner having the two concentrations tested, but in saline water it could be used up to almost 10 per cent salinity. If the suspected saline contamination is low the thinner can be used safely at a concentration below 0.3 per cent.

We may mention, finally, some research pursued in order to prepare a fungicide by heating sulfur in the presence of bentonite (Martín Vivaldi and Rausell Colom, 1955). The best temperature of treatment is 200°C, and 5 per cent of MgO is necessary to get stable suspensions, but with a particle size of less than 2μ no MgO is necessary, and the pH remains neutral. The sulfur must be, at least in part, between the layers of the silicate, as shown

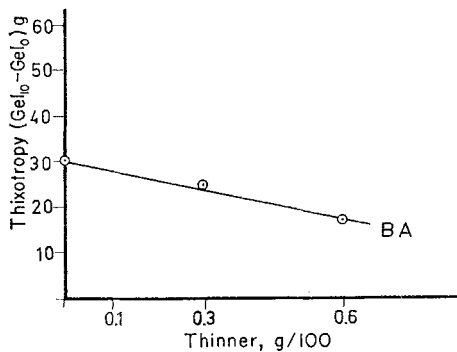


FIGURE 19.—Effect of A on thixotropy of Gadorgel suspensions.

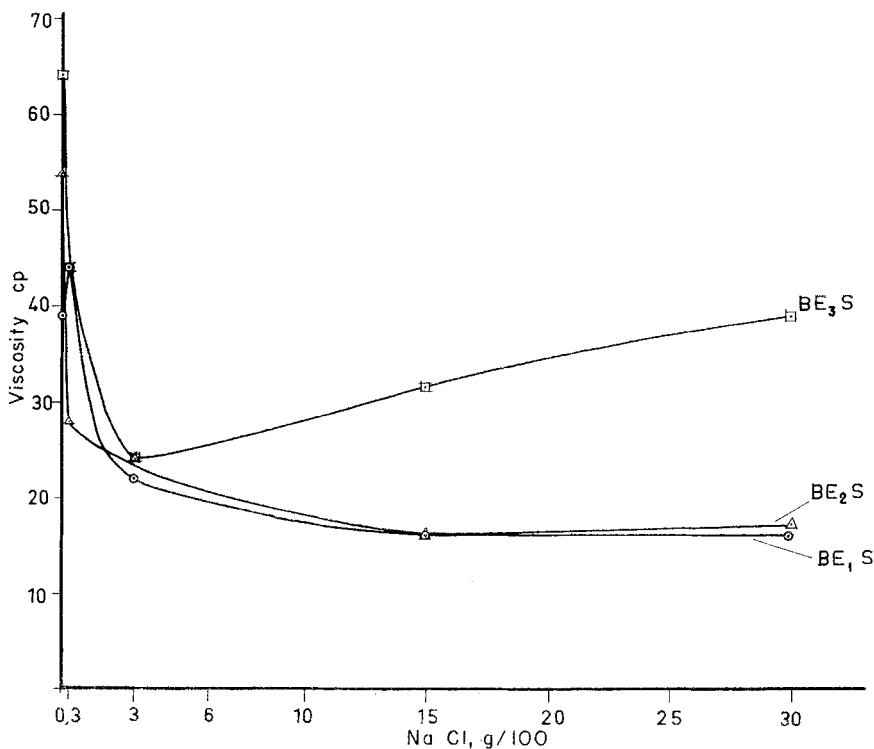


FIGURE 20.—Effect of NaCl on viscosity of Gadorgel suspensions plus E.

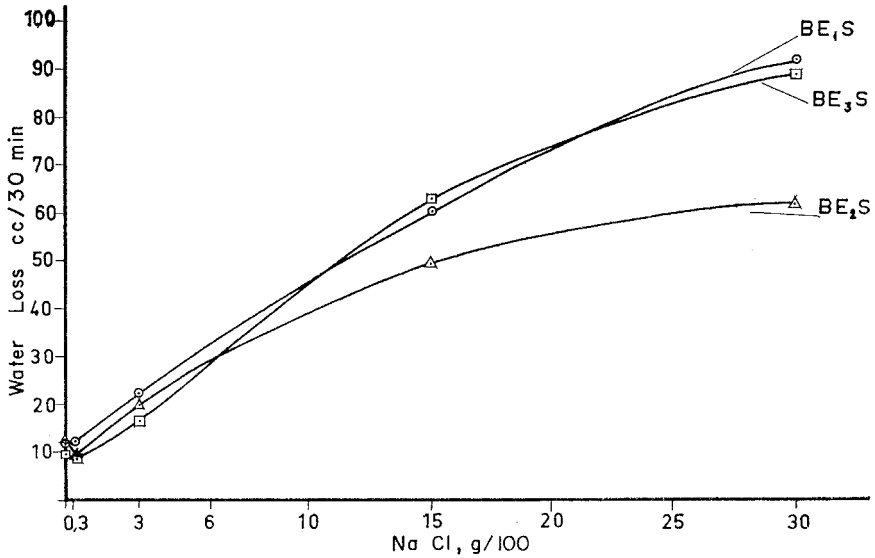


FIGURE 21.—Effect of NaCl on water loss of Gadorgel suspensions plus E.

by the X-ray diffraction photographs of heated samples. At any rate, the swelling properties of the bentonite with water and glycol are not affected (Table 10). Technically the product has very high activity as tested in the laboratory and in field experience (Tables 11 and 12).

TABLE 10.—*d* (001) SPACING OF BENTONITE AND ITS COMPLEX WITH SULFUR

| | Tidnit Bentonite | "Bentonite-sulfur" Complex |
|-------------------------|------------------|----------------------------|
| Untreated | 15.3 | ~ 15* |
| Dried at 110° | 9.8 ² | ~ 15* |
| Dried at 110° | — | 11† |
| Water treated | — | 19 |
| Ethylene glycol treated | 17.0 | 17.0 |
| Glycerol treated | 17.7 | 17.5 |

*. Band difficult to read.

†. Sealed in Lindemann capillary tubing to avoid rehydration.

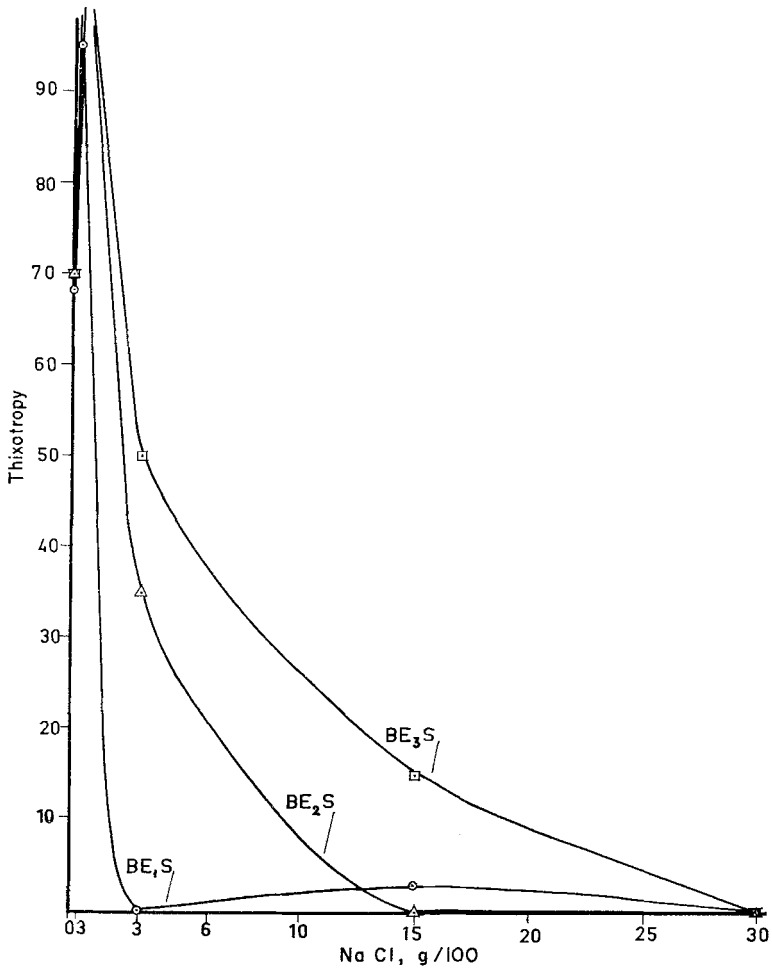


FIGURE 22.—Effect of NaCl on thixotropy of Gadorgel suspensions plus E.

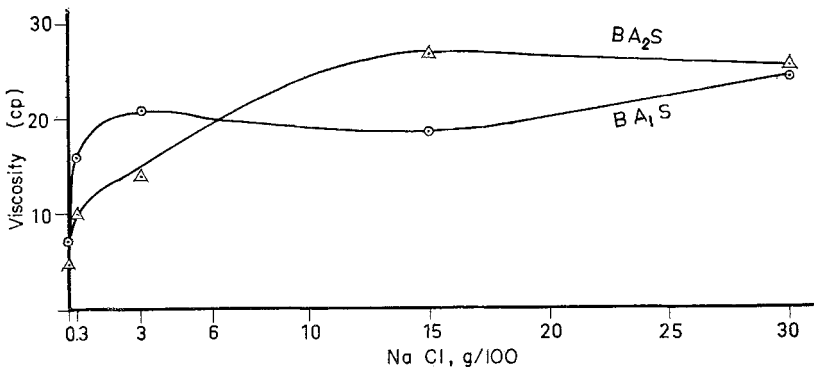


FIGURE 23.—Effect of NaCl on viscosity of Gadorgel suspensions plus A.

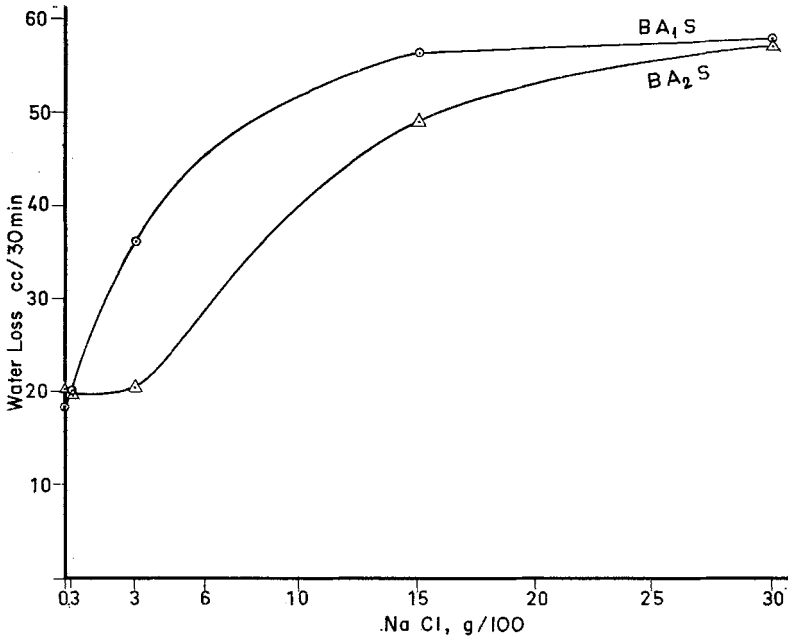


FIGURE 24.—Effect of NaCl on water loss of Gadorgel suspensions plus A.

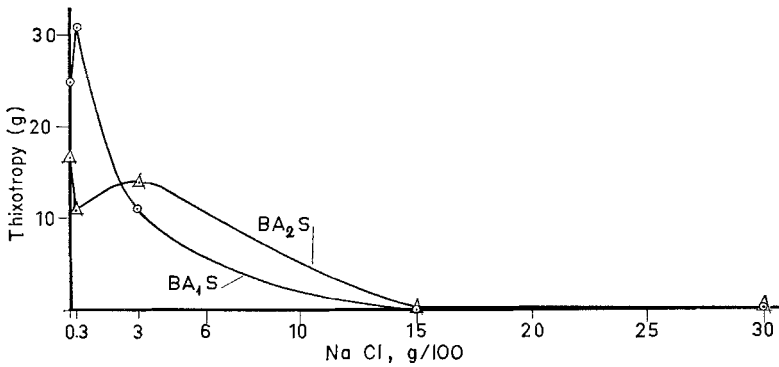


FIGURE 25.—Effect of NaCl on thixotropy of Gadorgel suspensions plus A.

TABLE 11.—EFFECT OF "BENTONITE-SULFUR" COMPLEX ON GERMINATION OF *Aspergillus sydowi* (Bain. and Sart.) THOM AND CHURCH

| Product | % of Spores Germinated* | Mycelium Tube Length (microns) |
|-----------------------------|-------------------------|--------------------------------|
| Sulfur complex with 33.3% S | 3.02 | 5-10 |
| Sulfur complex with 10.0% S | 3.70 | 5-10 |
| Sulfur complex with 5.0% S | 4.90 | 15 |
| Sulfur complex with 1.0% S | 6.55 | 15 |
| Ground Sulfur | 20.20 | 30-50 |
| Bentonite | 97.90 | 50-100 |

* 950 spores counted in each experiment.

TABLE 12.—RESULTS OF A FIELD EXPERIMENT WITH "BENTONITE-SULFUR" COMPLEX ON GRAPE VINE

| Fungicide | No. of Treated Trunks | g* Sulfur per Trunk | Infection |
|--|-----------------------|---------------------|--|
| Aq. suspension of sulfur complex containing 1.5 per cent S | 18 | 1.25 | None |
| Id., containing 3 per cent S | 18 | 2.00 | None |
| Sulfur powder | 16 | 60.00 | None |
| Blank | 6 | — | Strong, with <i>Uncinula necator</i> (schw.) Burr. |

* Calculated from the amount of suspension or sulfur powder, used in every spray, required for proper coverage of fruit.

ACKNOWLEDGMENTS

I wish first to thank the Clay Minerals Committee of the National Academy of Sciences—National Research Council and the University of Texas for their kind invitation to attend the Tenth National Clay Conference. I wish to thank also Prof. Fontboté (University of Granada) and Prof. Fuster (University of Madrid) for suggestions and help, and my collaborators—most of them mentioned in the bibliography—for their valuable experimental work. Finally I wish to express my high appreciation to "Minas de Gador, S.A.," for the kindness and facilities offered us during our repeated visits to their bentonite workings.

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