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Open-File Report 84-9F

Petrology and Genesis of Clinoptilolite in the Tallahatta Formation of Lauderdale and Clarke Counties, Mississippi

W. R. Reynolds

1984

The Mississippi Mineral Resources Inteitute University, Mississippi 38677

PETROLOGY AND GENESIS OF CLINOPTILOLITE IN THE TALLAHATTA FORMATION OF LAUDERDALE AND CLARKE COUNTIES, MISSISSIPPI

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Final Report for MMRI Project 84‡9F (including MMRI Project 83-5F) Submitted 21 December 1984 to James R. Woolsey, Ph.D. Director, Mississippi Mineral Resources Institute (Bureau of Mines Grant# G 1134128)

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The purpose of MMRI Project 84-9F combined with the results obtained through a previous field investigation supported by MMRI project 83-5F was to research the mining potential of sedimentary zeolites contained in strata of the 'Tallahatta Formation that is exposed in the vicinity of Meridian, Mississippi. The zeolite mineral found in this area which is used in a variety of industrial applications is clinoptilolite. Principle applications of clinoptilolite to mention only a few include its use as an agricultural food supplement in sewerage and waste water treatment, as a radio active waste containment, as a heavy metal extractant, as a paint extender, and as a whitener.

Sedimentary zeolites, by definition, are microcrystalline hydrated alumina silicates of alkali and alkaline earth cations. They are the product of diagenetic alterations or authigenic deposition in both open or closed marine and alkaline or ground-water sedimentary systems. Structurally zeolites are tectosilicates constructed of three dimensional totally polymerized alumina and silica tetrahedra. Such structural arrangement gives rise to numerous types of interstructural channel and cage configurations of varying sizes. Cations incorporated within these configurations through mainly hydroryl bonding are most commonly sodium, potassium, magnesium, calcium, and rarely strontium and barium. Clinoptilolite, one of the more common sedimentary zeolites, is a monoclinic silica-rich variety with potassium, sodium, and rarely calcium as dominant interchannel corporate cations.

Clinoptilolite occurring in Gulf Coastal Plain strata of southeastern U.S. was first found in Lower Eocene strata of Alabama (Reynolds, 1966) and Middle Eocene strata of Mississippi (Wermondtand Moiola, 1966). Later investigation in Alabama revealed clinoptilolite to be most abundant in the Middle Eocene Tallahatta Formation but also occurring in lesser quantities in the Lower Eocene Nanafalie Formation and the Paleocene Porters Creek Formation (Reynolds, 1970). Clinoptilolite has also been found in the middle phase of the Porters Formation of Mississippi (Raybon, 1982) and in the lower mud facies of the Porters Creek Formation of Tennessee (Sims, 1972). It was not until 1981 that clinoptilolite was discovered in strata of the Tallahatta Formation that is exposed in the vicinity of Meridian Mississippi (Reynolds, 1983).

Preliminary investigation of the Tallahatta Formation in the vicinity of Meridian, Mississippi supported by MMRI Project 83-5F involved lithologic description and measurement, sampling, and mineral determination of surface exposures of Tallahatta strata. This preliminary investigation provided substantial data by which an initial facies analysis was made, and it also revealed varying concentrations of clinoptilolite throughout the Tallahatta Formation.

The preliminary and field investigation showed that typically, within the study area (Figure 1), the Tallahatta Formation consists of three lithologic or sedimentation units (Figure 2). At the base, immediately above an unconformity between the Meridian and the Tallahatta Formations is, on the average, 15 feet (4.6 m) of transitional bioturbated glauconitic wackes and muds usually capped by two to eight feet of zeolitic clay (unit A). Lenticular to wavy bedding is most notable in both the mud and wacke strata of this unit and the surface between the lower unit and the upward succeeding unit is disconformable. The overlying unit (unit B) is what typically has been described as the Basic Shale even though it is not a shale but rather, for the most part, a massive soft to hard opal-Ct claystone (Lundegard and Samuals, 1982). This unit is, on the average, 45 feet (14 m) thick and contains thin lenses of zeolitic clay, however the massive claystone is often interrupted by upwards to 10 feet (3m) beds of mud and zeolitic clay. The uppermost unit (unit C) begins with either a mud facies or a glauconitic bioturbate opaline cemented wacke, and the average thickness of the entire upper unit is 44 feet (13 m). This unit consists also



2 1 N N N N N N

Figure 2a: Average lithologic composition of the Tallahatta Formation in the vicinity of Meridian, Mississippi.



Figure 2b: Exposure of Tallahatta outcrop seven miles south of Meridian on Valley Road. Units A, B and part of C are exposed overlying the Meridian Sand (M-lower right corner).

of alternating thin to massive, hard to soft opal-Ct claystone and zeolitic clay beds plus muds and wackes. Furthermore, it is usually capped by a thin often bioturbated arenaceous sand or sandstone.

The three lithologic units of the Tallahatta Formation, as described above, may vary in thickness and even arrangement but are fairly constant in content and can be traced throughout the study area (Roquemore, 1984).

One of the principal tasks designated as MMRI Project 84-9F is the description and mineral content analysis of eight cores taken with total penetration of Tallahatta strata at selected locations along the Tallahatta outcrop in Lauderdale and Clarke Counties, Mississippi. Drill site location (Figure 1) was based on outcrop exposure information. Data obtained from core analysis was coupled with exposure data in the effort to reconstruct the lithofacies of various depositional environments and subenvironments. Ultimately, when combined with mineral analysis, this would enable the derivation of a genetic model for clinoptilolite depositioned.

Core description and measurement (Appendix A) added information on lithologies and lithologic sequence within the Tallahatta Formation compatible with data obtained from outcrop exposure. Study of the cores provided the extra . stratigraphic control for lithofacies reconstruction. At each drill site approximately 150 feet of core was taken in 10 feet lengths starting in the Winona Sand, totally penetrating the Tallahatta and ending in the top of the Meridian Sand. Each 10 feet length was measured and described as it was pulled (Figure 3), then boxed and shipped to the University of Mississippi for further analysis. Elevation control for each measured section was maintained during field work by levelling from elevation monuments to the base of each exposed section to be measured and described . The position of each exposure section was also plotted on 7 1/2 minute quadrangles which allowed the qualification of subsequent adjustment of each basal elevation "brought" from various bench



Figure 3a: Describing core during coring operation at MCH 6.



Figure 3b: Ten feet of fresh core ready to be measured and described at core site MCH 6.

marks. This also allowed short sections (Figure 4) which represented scattered integral portions of a singular section to be brought together as a composite section. Each drill site was positioned by triangulation using a compass and the field vehicle tripometer. Drill site elevations were determined by using a pocket altimeter along with 71/2 minute, quadrangles for refinement and adjustment.

STRUCTURE

An initial stratigraphic section was constructed by "hanging" core and " exposure logs from a common datum of 500 feet above mean sea level along two cross-section traverses. One cross-section, AA, ¹ is essentially along strike, and the other, BB, is down dip (Figure 5). The tectonic elements in the study area turned out to be mainly a series of normal down-to-the-South faults (Figure 6) the movement of which involved the entire Tallahatta section with throws of 15 to 60 feet. The faulting events are not thought to be syndepositional but rather thought to have occured post Tallahatta, deposition. Only one fold feature, the Lost Gap Monocline, was ascertained (figures 4 and 6) as dips measured east to west along 120 from Meridian went from 0° to 15° and finally increased to 34° (Figure 4). More fold features probably exist in the study area but were not evident. Two of the faults can be seen visually in the field. One, between sections 51A and 49 is quite obvious as these sections are only 200 feet apart and the Meridian Sand in section 51A is juxtaposed to unit B claystone in section 49, which is a throw of about 45 feet. The second fault can be seen as a fault-line through unit B at the Basic City type section; a cut along the Illinois Central Gulf railroad one-half mile north of Basic City.

STRATIGRAPHY

Two palinspastic cross sections were constructed from the initial structural cross sections for the purpose of facies reconstruction (Figures 7 and 8).

These cross sections essentially summarize the stratigraphy of the study area. Even though the Meridian Sand was not considered a part of the operational unit of this study it has a few notable lithofacie characteristics pertinent to this study. The Meridian Sand is no longer the lower member of the Tallahatta but now is a separate formal unit (Dockery, 1981). It is quite evident that there is a distinct period of nondeposition of marine sediments between the arenaceous sands of the Meridian and the transitional muds and wackes of what is now the Lower Tallahatta. Throughout the study area the Meridian Sand for the most part is a clean medium-to fine-grained quartz arenite ranging from 100 feet (30 m) to 3 feet (0.9 m) in thickness. Weathered Meridian is either white or orange whereas fresh material is usually gray or brown where it contains organic material and is locally lignitic. The upper part of the Meridian is marked by a zone of intense burrowing with the unique cork-screw (Gyrolithes) and boxwork (ophiomorpha) burrows that are more resistant to erosion than the enclosing sand, and weather in relief.

Channel samples of the Meridian Sand were taken from exposures and cores for the purpose of grain-size distribution analysis. Probability plots indicate a polymodal grain-size distribution with an average phi mean of 1.75 and a strong predominance of the saltation population over a traction population (Appendix B). Most of the probability plots indicate a foreshore to nearshore intertidal beach as a general environment for the deposition of the Meridian Sand. However some plots along with cross-stratification data indicate very localized environments such as esturine, delta-plain fluvial and backshore subarea i beach (Visher, 1969; Roquemore, 1984 and Toulmin, 1966).

The lithologies of the Tallahatta Formation can be segregated into three lithofacies groups, and as previously discussed designated as units basically because each group is a distinct sedimentation unit. Unit A, the lowermost unit, consists of transitional wackes and muds and at least one distinct zeolitic clay bed. Unit B, the middle unit, consists of massive to thin bedded opal-Ct claystone. Occasionally, this unit will contain beds of zeolitized mud and zeolitic clay. Furthermore, the more massive claystone beds will often contain laminae (1/2" to 3") of zeolitic-opaline clay. The uppermost unit, unit C, consists of wackes, occasionally arenites, muds, silts and often thick beds of zeolitic clay.

Unit A (Figures 7 and 8) is thickest due South of Meridian (Section E45, Valley Road) but thins immediately to the West (E51, Basic City Type Section) then thickens to 35 (11 m) feet further west, and (MCH5, MCH7, C55) north-west, and thins again to the extreme north-west (MCH1). East of the Valley Road Section unit A thins to an average 10 feet (3m). Downdip this unit thins to a thickness of less than 10 feet (3m). Extensive bioturbation is a very characteristic aspect of this unit often halmarked by burrow mottling (Figure 9). Both vertical and horizontal, simple to complex burrows are plentiful in the wackes and muds of this unit especially if these beds are at the top (Figure 9). The common trace fossils include Ophiomorpha, Thalassinoides sp. and <u>Teeichichnus sp. of the Cruziana</u> association (Chamberline, 1978). Zeolitic clay beds in this unit are also heavily burrowed with individual burrows often preserved as opaline casts (Figure 9). Also notable within these beds are small segregated concentrations of sand usually circular or flaser-like in appearance (Figure 9). The wackes and muds are always glanconitic and micaceous. Channel samples were also taken in the lower unit A Sands for grain-size distribution analysis. Probability plots based on these analyses using dry sieve data indicate a mixture of depositional conditions, mainly deposition from suspension which is most common along barred coasts (Visher, 1969). Unit A is for the most part nonfossiliferous however occasionally a shell layer can be observed in the agillaceous sand near the top of the unit. Most common in this unit are plant fragments including large pieces of carbonized wood plus lenticular and wavy



Figure 8: Stratigraphic section BB' down dip A, B and C plus the underlying upper Meridian Sand and the overlying Winona and Zilpha Formations. Refer to Figure 7 for litholoev kev .



- Figure 9 : Unit A exposed in Valley Road section, section 45. Left: Wacke with opaline burrow casts and burrows of Ophiomorpha and Thalassinoid
 - Lower: Burrow mottling in unit C mud.

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bedding (Figure 10).

The principle lithology of unit B is a siliceous claystone composed of microcrystalline opal-Ct (Carver, 1980). The opaline strata appear to be massive but upon close examination they are in part laminar. Some of the strata however are thin bedded and have the appearance of a brick pile. Furthermore, some of the beds of unit B are soft and could be referred to as an opaline clay while others are highly indurated and form ledges. A few of the indurated ledges are highly fossiliferous with a dominance of the bivalves <u>Nucula</u>, <u>Nucul ana</u>, and <u>Venericardia</u>. Also notable in this unit, especially in core sections, are numerous thin layers (I^{M} to 6^{M}) of extremely brittle, sharp opaline chert.

Occasionally, wacke, mud and zeolitic clay strata are found in unit B. If any of these strata were found lithified the cement was either opal-Ct or clinoptilolite or both.

"Throughout the study area unit B varies little in thickness ranging from 30 feet (9m) to 45 feet (14m). It is at its thinnest in the Valley Road Section (E45) where it is 30 feet but immediately thickens to the East and the West.

The clays and claystones of unit B are olive-green to gray-green when fresh, but will bleach to a buff-gray or white when exposed. These clays and claystones have a distinct conchoidal to subconchoidal fracture, however the beds of pure opal-Ct are laminar the opaline material is extremely brittle and sharp. Surface exposures of this unit are quite distinctive, often forming steep cliff faces, vertical walls and pronounced ledges in road and stream cuts.

Primary structures found in unit B claystone include mainly small-scale cross-lamination, hummocky cross-lamination and stratification, lenticular and wavy bedding. Flaser bedding is often found in the wackes and muds along with small-scale cross-stratification. Lebensspuren are common throughout the unit, mainly in the wackes, and consists of unidentifiable horizontal tubes, and the ichnofossil Chondrites sp. (Chamberline, 1978) was identified in several cores.





Figure 10: Unit A exposures along Savoy Road Section 50:

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a) Carbonized wood in wackeb) Wavy beddingc) Storm surge bedding

A secondary structure, quite unique and most diagnostic in the more massive siliceous claystones, the zeolitic clays and some of the muds of unit B is that produced by sheet dewatering (Collinson and Thompson, 1982) (Figure 11).

The upper unit, unit C, is similar in lithology to unit A. However, it is thicker than unit A being at its 20 feet (6m) thinnest in the northwest sector of the study area (MCHI) and thickest, 80 feet (24m), in the south west portion. This unit is not exactly a mirror image of unit A even though it contains similar type muds, wackes and zeolitic clays. There are some clay beds in unit C that are not zeolitic but are rather opaline smectites. On the other hand the zeolitic clay beds are thicker and more abundant in this unit than in unit A. Also, in unit C are occasional aberrant opaline claystone beds. Beds of silt are also found in unit C but not in unit A. Like unit A the wackes and muds of unit C are bioturbated and contain plant debris, have hummocky stratification, and display lenticular and wavy bedding. These features, especially bioturbation, are not observable in outcrop exposures but are most diagnostic in the cored sections (Figure 12). One unique but not a common feature seen in the wackes of unit C is that of storms surge bedding; highly contorted and disrupted bedding (Figure 10). Storm surge sands in the road cuts of 120 (Section C55) underly a massive 12 foot bed of zeolitic clay.

The fine to coarse-grained, glauconitic, densely fossiliferous, calcareous and ferrugenous sand of the Winona Formation overlie unit C of the Tallahatta Formation. Exception to this is where Winona, Zilpha and to some extent Tallahatta unit C strata have been removed and replace by nascent Neshoba delta plain fluvial and delta front sands. These sands are generally coarse to medium-grained, quartzose and stained red. The Neshoba Channel Sands can best be seen in the 120 road cuts near the Chunky interchange, the valley road exposures (E45) and in core MCH 8.

The contact between the Winona Formation and the Tallahatta unit C is



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Figure 11: Sheet dewatering features:

- a) Petrographic thin section under plane polarized light of unit C clay. Dot scale is 25m«.
 - b) Same as a except from unit B
- claystone. Dot scale is 25m;4. c) Cross section of core from unit B claystone.



Figure 12: Examples of bioturbation seen in cores from units B and C.

everywhere conformable everywhere and is marked by a gradual change from clay or mud into glauconitic fossiliferous sand.

The Winona Formation in the study area is conformably overlain by the dark brown to black carbonaceous clays and silts of the Zilpha Formation which is a persistent unit throughout the study area. Often however, the Zilpha clays are lateral to the upper portion of the Winona Sand. These clays are massive, have a a conchoidal to blocky fracture, contain mica and glauconite streaks, and down-dip are fossiliferous (MCH 7). These bentonitic clays of the Zilpha Formation which also contain minor amounts of clinoptilolite are in turn disconformably overlain by the delta front and delta plain sands of the Kosciusko Formation.

Mineralogy

Previous field investigation involved in part the sampling of all Tallahatta clay beds exposed in the study area for determination of mineral content. Mud strata and selected wackes and opaline claystone beds and selected Zilpha clays were also sampled and analysed. Samples were then analysed by x-ray diffraction and scanning electron microscopy (SEM) for mineral content, mineral quality, and an estimate of mineral quantity.

The bulk composition of exposed Tallahatta clay, mud, wacke and claystone strata was found to consist of, in varying proportion, the zeolite mineral clinoptilolite, smectite (predominantly montmorillonite), coarse-to fine-grained muscovite, some illite, opal-Ct, and coarse-to fine-grained quartz (Figures 13,

14, and 15).

Material sampled from the cores also analysed in the same manner had a bulk composition identical to that of exposure material (Appendix B). Minor amounts of potassium feldspar and gypsum were also identified in some of the core samples.

X-ray identification of clinoptilolite was based on the presence of the



Figure 13: X-ray diffraction patterns of material sampled from clay beds exposed in section 45 (Valley Road).



Figure 14: X-ray diffraction patterns of material sampled from Zilpha clay exposed in sections 45 (Valley Road), 50 (Savoy Road), and 55 (120).

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Figure 15:X-ray diffraction patterns of material sampled from selected clay beds insections50 (Savoy Road) and 55 (120).

020, 004, and 042 reflections at 8.92 A°# 3.96 A° and 3.89 A° respectively. Diffraction patterns of smectite minerals are placed into two categories: 1) basal 001 reflections from 12.4 A° to 16 A°, and 2) hk reflections principally from 4.5 A° to 4.62 A°, 2.43 A° to 2.6 A°, 1.69 A° to 1.72 A°, and 1.49 A° to 1.54 A°. Basal 001 reflections are often unpredictable to use in Smectite mineral identification due to the varying influence of interlayer water, cations in exchange positions, and interlayer organic complexes. Often the 001 reflections are not evident when smectite is present because of layer disruption and disorientation due to large organic molecules being "stuffed" into the interlayer positions. On the other hand, hk reflections indicate smectite form and therefore, species. Montmorillonite was found to be the dominant smectite identified by diffraction traces of hk reflections at 4.5 A° and 1.5 A°. There was also indication of minor amounts of montronite and mixed layered illite-montmorillonite.

Jones and Signit (1971) have classified opaline silica into three structural groups designated as opal-A, opal-Ct, and opal-C. In an x-ray diffraction study of mixtures of opaline silica phases Tada and Iijima (1983) characterized and identified these structural groups using the (101) x-ray diffraction reflection. Diffraction patterns of siliceous clays from the Tallahatta Formation often had reflections from 4.06 A° to 4.1 A indicating opal-Ct which is consistent with Tada and Iijima*s results.

Muscovite was identified by its 002 and 004 reflections while quartz was identified by its 110 reflection.

Relative abundance of each of the dominant minerals per described exposure and cored section is shown as relative concentration in Zeta graphs coupled with lithology logs for each section - (Appendix C). Zeta graphs were constructed by assuming the sum of the selected x-ray diffraction peak intensities of the dominant minerals present in each sample would equal unity. Ratios of peak C

height were derived for each mineral in a sample and a standard, and were summed for each sampled section. The mean and standard deviation were computed for each ratio sum. The peak ratios were then standardize using a Zeta transform which resulted in new values where each ratio of peak intensity has a zero mean is expressed in units of standard deviation from than mean. This affectively allows a comparison of the relative mineral concentrations within a sample and between samples.

By examining the Zeta charts (bulk mineralogy) for each exposure and core logged section in Appendix C one can see some variance of clinoptilolite content within each section but less variance from section to section. The dominant occurrence of clinoptilolite in each section is in the upper clay bed of unit A and the one to three prominent clay beds of unit C. The variability of clinoptilolite content is shown more graphically in (Figure 16) which was constructed by determining the probability of occurrence of average relative mineral concentration between individual minerals within a stratigraphic unit (Figure 17) and plotting these values against stratigraphic position. This procedure subsequently enabled the construction of stratigraphic cross sections which are identical to Figures 7 and 8 except only the clinoptilolite-rich clay beds are correlated (Figures 18 and 19).

Clinoptilolite was detected in 88 percent of the samples examined by x-ray diffraction. Half of the samples taken from unit A have relative concentrations of clinoptilolite that are above average. Furthermore, clinoptilolite appears to be more concentrated in the muds and wackes than in the clays. Clinoptilolite occurs in 43 percent of the samples taken from unit B despite the fact that unit B composition is predominantly opal-Ct. In unit B above average relative concentration of clinoptilolite is found to correspond to above average relative concentration opal-Ct 26 percent of the time. This is probably due to the occurrence of extremely fine laminae of clinoptilolite clay alternating with



Figure 16: Relative mineral concentration of clays in units A, B and C of the Tallahātta Formation and the Zilpha Formation.

MICA CLINOPTILOLITE SMECTITE OPAL-CT QUARTZ

MICA	50	67	24	46
INOPTILOLITE		47	24	39
SMECTITE CI			28	29
OPAL-CT				18 ·
QUARTZ			j	

Figure 17: Association probability of above average relative mineral concentration as determined by x-ray diffraction pattern analysis.



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Figure 19: Concentration of clinoptilolite-rich clay strata down dip: cross section BB' (see figure 7 for lithology key). SEM analysis of selected sample material known to contain an above average relative concentration of clinoptilolite revealed this mineral to be cryptocrystalline with well formed monoclinic crystals (Figures 20 and 21) enclosed in what appears to be a pyroclastic matrix (Figure 20a).

Roquemore, 1984.

Upon closer examination it can be seen that the matrix is composed of authigenic montmorillonite (Figures 20b and 21a). Most often the submicroscopie crystals of clinoptilolite are nestled in clusters within vugs or pores which punctuate the matrix (Figure 21a and c). Clinoptilolite crystals and crystal clusters appear to grow either from the vug or pore wall or they seem to originate from the central portion of the vug or pore. These occurences offer three alternative explanations concerning clinoptilolite formation: 1) clinoptilolite forms from a material that made up the vug itself such as a siliceous microfossil or volcanic glass, 2) the initial material was dissolved creating the pore space and clinoptilolite grew from a material introduced later, 3) or clinoptilolite precipitated from connate pore fluid.

The form of clinoptilolite crystals in the Mississippi materials is more like a potassium feldspar rather than henlandite (Reynolds, 1983). Often one can observe twinning of clinoptilolite crystals of either the carlsbed or manebach type. Furthermore, it appears that soon after a crystal has formed it begins to deteriorate (Figure 21a, c and d). It has recently been suggested that clinoptilolite deposits in humid areas such as the Coastal Plain of Southeastern United States are comprised of crystals formed in fluid filled pores which may or may not be relict bubble structures. Crystal growth proceeds to a point when there is a change in pore fluid chemistry at which time the fluids attack the crystals producting crystal degradation (Reynolds, 1983).

Figure 20

a. Section 55A (Interstate 20) Sample 80.10 320x Magnification
Low Magnification SEM surface sean of material from the upper zeolitic clay bed. Surface appears to have a relic pyroclastic texture.

 b. Section 55A (Interstate 20) Sample 80.10 7780x Magnification High magnification SEM surface scan of authigenic montmorillonite.

c. Section 45 (Valley Road) Sample 53.33 5238x Magnification SEM identification of a well formed clinoptilolite crystal with no indication of crystal deterioration.

d. Section 55A (Interstate 20) Sample 80.10 21400x Magnification SEM identification of a clinoptilolite crystal showing well formed 010, 110, 101, and 100 faces.









Figure 21

a. Section 55A (Interstate 20) Sample 80.10 4000x Magnification SEM micrograph showing different states of clinoptilolite crystal deterioration. The three crystals of interest, marked with c, are encased in authigenic montmorillonite. The Crystal at the upper left shows little alteration, the central crystal shows the effects of severe leaching, and the crystal in the lower right has undergone almost total deterioration.

 b. Section 50 (Savoy Road) Sample 69.76 22470x Magnification SEM micrograph of well formed clinoptilolite crystals. Note at left side of photo the beads of incipient montmorillonite along a crystal face boundary.

- c. Section 52 (Arnndel) Sample 76.1 644x Magnification SEM micrograph showing a cluster of clinoptilolite crystals in various stages of deterioration.
- d. Section 52 (Arnndel) Sample 76.1 2600x Magnification
 SEM micrograph of c above at increased magnification to show incipient montmorillonite in the form of "toothpaste" and "sheet" structure along cleavage planes.



<u>13 pn</u>

1/2 µm

С

11 i. fs n o t k n o w n p r e s e n 11 y w h e t h e r o r n o t t h e T a 11 a h ;à 1.1 a c Mississippi i si produced from the alteration o-f a volcanic precursor. The montmorillonite observed occurring with the clinoptilolite is possibly an initial authigenic product from the alteration of volcanic ash. If this is the case, clinoptilolite then is a later formed product growing in pore spaces provided by relic bubble structures. On the other hand, close examination of clinoptilolite crystals in various stages of deterioration reveals incipient montmorillonite in the forms of "beads" (Figure 21a) or as "toothpaste" lines (Figure 21a and c) and "sheets" (Figure 21d) along either crystal face boundaries or cleavage plane junctures.

M IN E B A L O C C U R R E N C E

X-ray and SEN investigations were significant in determining the existence of clinoptilolite besides crystal morphology and to some extent mineral quantity in material sampled from wackes, muds and clays of the Tallahatta Formation. These analytical methods however did not lend much insight into the modes of mineral occurrence or mineral genesis. Therefore, for this phase of investigation it was decided that in addition to x-ray and SEIM analysis there should be a return to the "basics"; petrography.

Petrographic characterization of clinoptilolite was based upon optical e x am i nat i on o f t h i n-sect i ons pr ep a r ed using out c r op e x pos ure and cor e samples b o t h the T ¿A 1 1 a h a 11 a a n d Z i 1 p h a F o r m a t ions. T o c o m p 1 e m e r 11 t h e t thirty samples were disaggregated, separating the coarse fraction (62 urn) for optical examination in immersion oils with refractive indices of 1.54. Samples were selected for thin-section examination based on mineral content as revealed by examination of x-ray data. The samples were selected to represent differentcombinations of zeolite concentration and mineral association, and minerals were identified using standard optical methods.

Detailed petrographic description of each thin-sec tion and grain mount was

beyond the scope and purpose of this study. Rather, a summary of the general characteristics of both thin-sections and grain mounts is presented here, with thi petrographi (I characterofc linoptilolilereceiving a more de

The detrital component of the thin-sections studied consisted mostly of angular silt-sized quartz grains, crudely oriented laths of white mica, and more rarely alkali feldspar. The ground mass consisted of smectite and opal-CT (verified by x-ray diffraction). Texturally the samples are muds, silts and clays, as material coarser than 62 microns was not common. Bright green glauconite grains occurred in all thin-sections and most grain mounts. Usually these grains were elipsoidal to spherical in shape and of uniform size. Rare subhedral glauconite grains were also observed. Occasionally the elipsoidal and spherical glauconite grains are with cracks filled with a matrix material, probably opal-Ct. Glauconite was also found to replace organic remains such as the central canals of sponge spicules. Pyrite was found in most all the thin-sections and grain mounts, and was usually associated with organic material and often occurred as single cubes or framboidal masses. Completely pyritized microfossils of diatoms, sponge spicules were observed. Opaque to semi-opaque organic material was common in the smectite-rich samples. Microfossils are abundant in all samples and consist mostly of diatoms, sponge spicules and more rarely r ad i o 1 ar i ans. Calcareous microfossils, mostly chambered f orami ni f erans and some calcareous algae were observed in a few samples. The most common accessory h e av y mine ral s ob served i n cl u ded r ound ed z i rcon, horn blende and s t auz ol ite, a n d rarelyphiosphategrains.

In both thin-sections and grain mounts clinoptilolite exhibits prismatic and tabular crystals having a monoclinic outline (Figure 22c). These crystals range in size from barely discernible under highest magnification to well -formed crystals up to a maximum of 40 microns. Average crystal size was about 15 to 20 micrometers. Observed clinoptilolite has a refractive index of approximately 1.48 Fage 1



and for c is 25m/-..

which is in agreement with the index given by Boles (1972) and Mumpton (1960). Under pl sin light clinoptilolite is colorless to light violet and has a strong negative relief. Under crossed polarizers clinoptilolite shows dark to pale grey -firs t - orde r i n t e r f e r enee co .1. or. This t e n d e n c y f o r ci a r k i n t e r -fer the small size makes optical determination difficult in thin-sectior though a well-formed biaxial figure can be obtained with difficulty from some crystals. Clinoptilolite crystals were usually euhedral, commonly twinned and inclusion free. Corrosion of individual crystals is apparent, in some samples, though it it not common.

Clinoptilolite observed in thin section and grain mounts from the operational units in southeast Mississippi has several different petrographic modes of occurrence, which are classified into the following groups.

(1) . Clinoptilolite occurs as matrix-cement of silt to sand sized particles, an occurrence which could only be observed in thin-section (Figure 23). The clinoptilolite in this category appears to grow within the pore spaces between angular particles of quartz, occasionally mica, and rarely feldspars. Other particles making up approx i matei y 5 to 10 percent of the coarse fraction include abundant sponge spicules and diatoms and more rarely radiolarians. Glauconite grai ns and opaque organic particles were also present in the coarse fraction. Where other matrix material was associated with clinoptilolite, opal-CT was more common than was smectite. One should note in Figure 23 the sharp angularity and embayment of quartz particles. These particles more often than not exhibit straight extinction. Both of the above aspects suggest the quartz to be volcanic. Also, in Figure 23 note the wavy or undulóse structure of the clinoptilolite matrix which appears as a pyroclastic fabric similar to authigenic montmor illonite.

(2) . Clinoptilolite occurs as a mineralization product within dewatering veins and sheets (Figure 11) where it either fills the veins or sheets or only

Fage lć





Figure 23: Petrographic micrographs showing pyroclastic fabric and clinoptilolite infilling of microfossils (upper) and clinoptilolite as a cement (lower). Dot scale is equivalent to IOOung.
lines the perimeter (Figure 24c). It appears; that clinoptilolite growth proceeds from the vein or sheet wall inward which suggest preci pi tati on from fluids moving notonlythroughbut intot. heveins and sheets.

(3) . Clinoptilolite occurs as a replacement material in voids of microfossil! and shell fragments. These voids are formed by the dissolution of diatoms, spongi spicules, forami niferans and radiolarians are often filled by blocky crystals of clinoptilolite whereas others seemly have converted to opal-CT (Figure 23). Replacement involves dissolution and reprecipitation which destroys most of the textural aspects of the microfossils even though the relative size and shape remain the same. Grain mounts offer a better means of observing the replacement. type of clinoptilolite growth which seems to be toward the center of such voids Pyrite is neari y always found associated with clinoptilolite within these voids.

(4) . Clinoptilolite occurs as a direct transformation product of siliceous microfossils. This mode of zeolite occurrence involving siliceous microfossils was very apparent with optical examination of grain mounts. Clinoptilolite o c c u r r e n c e i n t h i s m a n n er s u g g e s t s t. h e a p p ; A r e n t d i r e c:: t t : microfossils to the zeolite without involving dissolution since the external structural integrity of the microfossil is retained (Figure 25c). This also may suggest material packed into the microfossil test after death and subsequently converted to clinoptilolite.

(5) ., The prominent occurrence of clinoptilolite is in large pore spaces (Figure 24a and b) where crystal clusters are seen growing from the walls or the central p or ti ons of the pore spac es. Thi s occurr enee li ke that i n dewater i ng viens and sheets suggests clinoptilolite precipitated from fluids either that have moved through a buffering matrix into the pore spaces or were already occupying the pore spaces and responded to a physical stimulus such as temperature change and/or compaction pressure.

. Clinoptilolite occurs as an encrusting material on detrital grains.

(6)

Fage 1



Figure 24: Petrographic micrographs showing clinoptilolite infilling large vugs (a and b) and dewatering veins (c).

This final category is most obvious observed in grain mounts rather than thin section. Here, clinoptilolite crystals encrust, quartz, mica and possibly feldspai grains, and there appears to be no dissolution, alteration or transformation involved between the clinoptilolite and the detrital mineral grain (Figure 25a ant b). This association indicates clinoptilolite probably grew into pore spaces surrounding the detrital material from the grain surfaces thus becoming the grain to grain cement of the lithified wackes and muds (Figure 26).

Th i n-sect i on and grain mount, examination revealed no conclusive textural evidence to suggest a precursor pyroclastic material ever being present in the Lower Claiborne sediments of southeast. Mississippi. According to Ross (1928) and Ross and Smith (1961) pyroclastic sediments have characteristic structures produced by the fragmentation of globular bubbles which produce curved plates, cusp and lunate shaped, and Y and U shaped shard particles. In addition, a definite mineral association is often present including: idiomorphic zircon, euhedral brown biotite, euhedral quartz with embayed structure, subhedral sanidine with irregular embayed fractures, hornblende and pyroxene.

Authigenic feldspar was identified in some samples, usually first revealed by analysis of x-ray patterns.. A cursory examination of fine sand from various positions in the Basic City showed a surprising abundance of sponge spicules and diat o m f r u st u 1 es associat e d w i t h z e o 1 ite. 01 h e r , p e r hi a p s u n u s u a 1 , n o t e d i n d i s a g g r e g a t e d Z i. 1 p h a a n ei s o me T a 11 a h a 11 a s ¿i m p 1. e s aggregates of sponge spicules surrounded by matrix of light brown (clay mineral) material are commonly observed. These aggregates also contain bright green glauconite part, ici es, quartz grains and opaque organic materials. Disaggregate feature. Close inspection of individual "grains" in grain mounts indicated they were composed of skeletal fragments of diatoms and or radi olari ans in a pale brown cement.

Page 1.

Figure 25 : Photomicrograph of grain mounts showing.



а

Clinoptilolite encrusting a mica grain. Dot scale is equivalent to 50m¿<.

b

Clinoptilolite encrusting a quartz grain. Dot scale is equivalent to 50m/x.

С

Clinoptilolite completely enclosed within a radiolaria test. Dot scale is equivalent to 25tm>n.

CLINOPTILOLITE AS A CEMENT

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EE v e n t h o u g h t h e ¿a n c:: i e n t M i ss i s s i p p i e m t) a y m e n t. w ¿a s g e t. h e c: h a r a c t. e r i s t i c ss c J f s e dime n t. a t i. o n p t- o c. e s s-s e ss and r e •found along the mesotidal coast of a shelf sea with incorporate depositional environments as tidal flats, barred coastal areas, open beaches and nascent deltas. During Wilcox and early Claiborne time the western and northwestern portions of the embayment were lined with large coalescing delta complexes (Duplantis 1975). On the other hand, along the eastern and southeastern portion smaller Wilcox deltas easily gave way to wave dominated coasts which seaward boardered a broad shallow marine shelf.

The lithologic units of the Tall ahata Formation in the area of Meridian, Mississippi reflect, a marine transgr essi on-r egressi on cycle, beginning in the upper Meridian Sand and continuing into the Koscinsko Formation. Mainland beach, barrier beach, delta front and tidal flat sands of the Meridian Formation give way to transi ti onal wackes and muds of an early Tallahattaa marine transgression from the southwest and extending beyond Meridian, Mississippi. The transgressive processes abated during the middle tallahatta with the deposition, under low energy conditions, of siliceous clays over a broad tidal flat shelf. During this time however were numerous short periods of coastal progradation and retrogration r e p r e s e n t e d by sediment dis t r i b u t i on c h ara c t e ri st i c o f n u m e r o u s s local li zed transgressions and regressions.

The lithofacie associations observed in the upper tallahatta suggest this time to be a period of marine regression. This was a time when coastal nearshore and foreshore plus nascent delta environments moved seaward to the southwest over the previous broad tidal flat shelf. The thickness of unit ft strata indicates the regressive phase to have occupied more time than the transgressi ve phase. However, there is little evidence in unit ft strata that suggests rapid tr ansgr essi on. The difference must lie in the aspect that more t err i geneous material was supplie eit. ot he deposition a la re a ísduri. ngt here gro durirīg the transgressivephase-С 1. .j. D. 9 P. tí L Q1 í. tæ Е С! ЕФЕ́т. Ł Q П

Obviously the tal .1 ahat, t a sedimentsrepresent a period of extensive silica deposi ton. The initial deposition of silica would have been in the form of opal-C (Carver 1980) which presently is undergoing transformation to quartz through the opal-Ct phase. Deposition of material eventually altered to clinoptilolite was apparently concomitant in time to the deposition of silica. Sites of clinoptilolite precursor deposition appear to have been segregated subenvironments on the shelf and along the coastal regions. Such segregated sites include a variety of entrapment depocenters, mainly nearshore runnels, lagoonal troughs, anc back barrier inter t.idal zones.

Cryptocrystalline clinoptilolite crystals disseminated in argillaceous sediments consequent with the occurrence of clinoptilolite as much larger euhedral crystals in-filling varaus microfossil voids, sponge spicules and anomalous vugs and pores suggest clinoptilolite to be an authigenic mineral formed through preci pi tation from interstitial solutions. Furthermore, clinoptilolite growth in dewatering veins and sheets and as a cement, matrix suggest, post-burial migration of pore solutions prior to clinoptilolite formation. Growth of clinoptilolite within diatom and other siliceous fossils could be evidence for direct, in situ transformation with no apparent dissolution and reprecipitation phase (Curtis and Cornel 1 , 1972; Fan and Zemmels, 1972; Burger and van Rad, 1972; Lancelot, 1979; Houghton, et. al. 1979; and Riech, 1979).

There is only scanty petrographic evidence that volcanic ash was a major source of si lica in the Tallahatta and Zilpha sediments. This may be due the fact that in nearshore environments strong currents and high production of biogenic material may have rework, redi str i bute and dilute pyroclastic material so that it is less easily recognizable in these types of deposits (Hathaway et al, 1970). Boles and Wise (1978, p» 239), discuss the occurrence of clinoptilolite in deep-sea sediments and suggest, that if clinoptilolite is formed only from glass then the majority of clinoptilolite occurrences should be associated with ash beds, and concluded that the majority of deep-sea clinoptilolite is not associate! with volcanic glass. Furthermore, Kastner and Stonecipher (1978) report that onix twenty to twenty-five percent of the deep-sea clinoptilolite occur in sediments that are prdominantly volcanic.

The presence of abundant siliceous microfossils in various stages of dissolution somewhat supports the hypothesis that they contributed to the vast, amount of silica deposited during Tallahatta time. Hein et al. (1978), in a study of sediments from the Berincj Sea, derived a similar hypothesis for ¿A biogenic contribution to the formation of clinoptilolite in those sediments. .pa The absence of petrographic evidence of pyroclastic material in Tallahatta sediments does not however preclude the existence of such. Perhaps a cause-and-effect relationship between volcanic activity and biogenic deposition is possible. Reynolds (1970) has pointed out that the clinoptilolite-rich strata in the fall ahatta Formation of Alabama may have had a volcanic precursor, but also suggested that volcanic ash could not have been the precursor of the opal-CT.

In this study it was found that clinoptilolite is more likely* to be associated with detritial sediments than with large amounts of opal.....CT. This relationship suggests that clinoptilolite formation is more favorable in sediments with some terrigenous input while? opal-CT formation is favored when there is a minimum of terrigenous input. Kastner et al., (1977) has shown that the rates of dissolution of opal-A (biogenic) and recrystallization of opal-CT is inhibited by the presence of clay minerals. Houghton et al. (1979), reports that high c a r bona t e con t e n t p r o h i b its c l i n o p t i l o l i t e g r o w t h a n d e v e n p r dissolution. Nathan and Flexer (1977) have noted the negative correlation between opal-CT and clinoptilolite and suggest, that clinoptilolite formation is favored by hi.gherthannorma J. concentratons of ma.gnesium.

Tradi ti onal 1 y Zeolite -formation is considered as an alteration process of volcanic, glass; a concept well documented for most categories; of zeolite occurrence in a variety of sedimentary environments (Hay, 1978). In this study however field and laboratory investigation failed to produce strong evidence of a volcanic ash precursor for clinoptilolite formation. This does not suggest, however, that the volcanic precusor was not there. Alternatively, results of petrographic study show that a biogenic contribution of silica was possible as clinoptilolite has been observed in void spaces provided by dissolution of siliceous as well as calcareous microf ossi is. Therefore, it seems plausible to suggest that clinoptilolite in Tal ihatta sediments may owe its origin, at least in part, to silica derived from the dissolution of siliceous organisms. Stratigraphic positioning and mineralogic relationships by the simplest of interpretation indicate clinoptilolite formation is more favorable when a clastic component has diluted biogenic sediments, whereas opal-CT formation is more likely in sediment havei ng a greater proportion of biogenic silica.

The major source of silica is thought to be the same for both clinoptilolite and opal-CT formation, and deposi tonal environment is thought to have played a significant role in influencing the formation of either mi neral. The absence of opal-CT in the zeolitic beds of both unit A and unit C is thought, to have resulted from a number of factors. First, in the lower and upper beds of the Tallahatta a g r e a ter- c o n t ent o f c-o a r s e - g r · a i n e d m a t e r i a l prod u c e s h i g h e r p porosity and permeability which could have enhanced the formation of clinoptilolite by allowing easier migration of reactive ions in silica-rich fluids. The upper and lower units are also highly bioturbated, which suggests organic activity may have been an effective agent for clinoptilolite formation. Finally, pyri tized organic material such as plant remains and diatom frustules indicate reducing post-depositional conditions.

Page 2:

The one discrepancy concerning clinoptilolite formation from siliceous biogenic materi al is the lack of an apparent aluminum source. In the case where clinoptilolite forms from a volcanic precursor this source is readily apparent. However, diatom frustules and other siliceous microrganisms are reported to contain only a minor amount of aluminum (0.5 ppm). Hein, et al. (1978) support a biogenic source of silica for clinoptilolite formation, but suggest that the reacting system in which clinoptilolite forms must derive its necessary aluminum through the dissolution of amorphous clays.

Their work suggest that diatom debris, already covered with clay-like minerals, might serve as nucleius for authigenic mineral formation such as clinoptilolite. Smectite has been reported to be present in living diatoms the frustules of which are reported to contain up to 1.5 percent aluminum (Van Bennekum and Vander Gaast , 1976). This may suggest diatom debris, already covered with clay-like material, might serve nucleus for authigenic mineralization as а such as clinoptilolite formation.

When considering all of the evidence it seems highly unlikely that dissolution of siliceous microorganisms would provide an adequate amount of necessary ion constituents to form clinoptilolite. Evidence is strong however for the preci pi tation of clinoptilolite from interstitial fluids. From where do these fluids incorporate, to a state of saturation, the necessary ions? Detrital clay h as been one s u g g e s t ion. U n f o r t u n a t e 1 y mos t o f t he s m e c: t i t e o c c u clinoptilolite is also authigenic. Clay and zeolite can form from the same precursor material which is evident in the recent Mt. St. Helens ash falls (Revier 1982) ..

Mol for mol clinoptilolite is composed of the same ions found in ryolitic ash however, montmorillonite requires only half the silica and some magnesium (Reynolds, 1970). Therefore, montmorillonite could be produced by the deterioration of the first formed clinoptilolite which originated by precipitation

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+ r om pare waters enriched by the dissolution o(volcanicash.

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APPENDIX A

CORE LOGS

CORE LOG KEY

LITHOLOGY

ALPHA NUMERIC

		Al	MICACEOUS	G13	CLAY PEBBLES
	CLAY	Ala	SLIGHTLY MICACEOUS	G14	SILT BLEBS
		A2	GLAUCONITIC	G1.5	SILTY
		A2a	SLIGHTLY GLAUCONITIC	G16	OPALINE BLEBS
		A3	PYRITE	010	
	SAND (WACKE)	A 4	OPADINE	нl	SAND FIACEDS
		A 5	OPALINE CEMENT	и2	
4 4		A 6	CHERTY	112	DEDING
		77	CVDSIIM	11.2	BEDDING MANY DEDDING
	SAND (ARENITE)	78	FEDDUCENOUS		WAVI BEDDING
		AO A Q	ADCILLACEOUS	H4	SAND BLEBS
777		A9 710	ARGILLACEOUS CAL CADEOUC	HS	SANDY
17	ODALTHE CLAV	AIU	CALCAREOUS		
	OFALINE CLAI	D			
		B	FOSSILIFEROUS		
		BI	BIOTURBATED		
	CLAYSTONE OPAL CT	B2	PLAN'I' REMAINS		
	olificational office of				
		CI	MASSIVE BEDDING		
~~		C2	LAMINAR BEDDING		
\approx	SILT & SILTSTONE	C3	TRANSITIONAL		
		C4	DENSE		
# # #		DT	DIOCUY		
# #	CHEDT	DI	BLUCKI		
	CHERI	DZ	CHONCOIDAL		
		D2a	SEMI-CHONIOIDAL		
		D3	FRONDESCENT OR VEIN STRUCTUF	Ε	
	MUD	D4	MOTTLED		
		D5	CROSS LAMINATION		
		D6	FISSIL		
	SANDSTONE	E	SECONDARY SULFATES		
+ + +		F LIG	NITIC		
+ - +	MUDSTONE				
		Gl	COURSE TEXTURE		
		G2	MEDIUM TEXTURE		
		G3	FINE TEXTURE		
		G4	PLASTIC		
		G5	WAVY		
		G6	SILT LAMINAE OR STREAKS		
		G7	SAND LAMINAE		
		G8	CLAY LAMINAE		
		G9	BRITTLE		
		G10	SHARP		
		G11 C	LAY BLEBS		
		G12 0	UARTZ PEBBLES		
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 Baseri, apil, E., tatturel anit-bil
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FRODABILITIES ÜF SAND-SIZE POPULATIONS

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Cumnulative probabilities of sand-size populations of the Upper Meridian Formation. Section 57 (Mt. Barton): a, b, c Section 55 (1 20): d



Curamulative probabilities of sand-size populations of the Upper Meridian Formation. Section 45 (Valley Road): a, b Section 50 (Savoy Road): c, d



Cummulative probabilities of sand-size populations of the Upper Meridian Formation (section 51» Highway 111 a, b, c) and of the Lower Tallahatta Formation (section 55? 120; d).



Cummulative probabilities of sand-size populations of the Lower Tallahatta Formation (section 49; Basic City: a, b) and of the Winona Formation (section 45; Valley Road: c, d)

APPENDIX C

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MINERAL DULK COMPOSITION





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- P PLANT FRAGMENT
- T TRACE FOSSILS
- W DEWATERING VEIN
- X CROSS LAMINATIONS L LAMINATED
- C CHERTY

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	А мт мб tro trw- 15>w iU w 15500-		но inf Патанова я4я0яв сатанова	AUW-CIII >TP- IMTR IMTR IUW-Bi IUW-Bi IUW-Bi IUW-Bi IUW-Bi Bi DI Or > M HICANY	M, 01, 14, At, At, oto H, ás, Al, 010 M, st. TM STLIXAY SVA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), oio C. 61, 617, AL, AL, AL, AL, M M, ote, оцимиви), oio C. 61, 617, AL, AL, AL, AL, M H, ote, outimer, and an and a state u otaw M-01, 05, At, Ai, >1, oto N, 01, 05, At, Ai, >1, oto N, 01, 01, 51, AI, AO, M B, ci, At, u.an. ei, au, M. S, 01, AI, AO, Otf M, at, at, k Doom, MmoOl At, AO, It C, Ch, C, off AD, M
	мт мо*« мf tro trv- 15»w- ии ии ии ии ии ии ии и		но inf CLAYRORE R4Я0ЯВ CLAYRORE CLAYRONE CLAYRO	auw-ciii >TP- Im-Si IMTR III	M, 01, 14, At, At, oto H, <u>as</u> , <u>AI</u> , 010 M- <u>st</u> , <u>FM</u> , <u>01</u> , <u>AV</u>
	Mo*« Mf tfo*- tfo*- tfu 15>w 15500- 15500- 15500- 15500- W 15500- W		но inf CLATERCE R44909B CLATERCE CLATE	auw-cin >TP- IMTR III W-Bi III W-BI IIIII W-BI III W-BI I	M. 01, 14, At, At, oto H, ás, Al, 010 M. 51, H, J., At, At, oto H, ás, Al, 010 M. 51, H, STL (ЖАУ ЗХА BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), oio CL 01, 05, At, AI, AT, AT, AT, AT, AT, AT, AT, AT, AT, AT
	MT MO*« Mf tfW- 15>w- IU W '15500- 1350 MO'' UI		но inf PA4909B CLATEROE CLATE	auw-cin >TP- IMTR III TP- IMTR III TP- IMTR III TP- III TP- IIII TP- III TP- III TP- III TP- III TP- IIII	M, 01, 14, At, At, oto H, ás, AI, 010 M-51, M, JI, XA, SIA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцммви), oio ct. 61, 617, A1, A2, A5, 31 te aheve u otaw M-01, 05, At, Ai, >1, oto Noj [] [] [] [] [] [] [] [] [] [
	A MT Mo*« Mt tto ttw- 15>w- iU w 15500- 150^ w- 150^ W 150^ W 150^		но inf IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	auw-cin >TP- IMTR IMTR IUw-Bi IUw-Bi IUw-Bi Iuw-Bi Iuw-Bi Iumai Immai Iumai Immai Iumai I	M, 01, 14, At, At, oto H, ás, AI, 010 M-SL: M STL (XAV StA
	A MT Mo*« Mi tro- trw- 15»w- w 15500- 150 150 150 150 150 150 150 150 150		но inf CLAYFORE CLAY	auw-ciii >TP- Im-Si IMTR III	M, 01, 14, At, At, oto H, <u>as</u> , <u>AI</u> , 010 M, <u>si</u> , <u>AI</u> , 010 M, <u>si</u> , <u>AI</u> , <u></u>
	A MT Mf tfo"- tfv- 15>w- 15>- 15500- 15500- 15500- 15500- 15500- W- 15500- V- NO UI		но inf CLAYBOOR CLAY	auw-cini >TP- IMTR III	M. 01, 14, At, At, oto H, as, Al, 010 M-51 = M SUL (жА) SUA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), oio CL 01, 05, AI, AI, AJ, AJ, AJ te aheve u otaw M-01, 05, At, Ai, >1, oto Noi () $(i > 1, AI, AJ, AJ, AJ, AJ, AJ, AJ, AJ, AJ, AJ, AJ$
	MT MO*« Mf tfW- 15>w- IU W '15500- ' ' ' ' ' ' ' ' ' ' ' ' ' ' ' ' ' '		но inf CLATERCE R44909B CLATERCE CLATE	auw-cini >TP- IMTR III W-Bi III W-BI IIII W-BI III W-BI I	M. 01, 14, At, At, oto H, ás, AI, 010 MSI, M. STLUXAV SIA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), olo C. 01. 017. AI. AZ. AS. 31 te aheve u otaw M-01, 05, At, Ai, >1, oto NOI () () () () () () () () () (
	А MT MO*« HO ttw- 15»w- ии 15500- 15500- 15500- 15500- 150 м мо ии		но inf PA4909B CLATEROE CLATE	auw-cin >TP- IMTR III T	M, 01, 14, At, At, oto H, ás, AI, 010 M-SI, M, JI, IX, AV, SIA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, ouµммви), oio C. 91, 917, A1, A2, A5, 31 te aheve u otaw M-01, 05, At, Ai, >1, oto N 01, 05, At, Ai, >1, oto N 01, 01, >1, AI, AO, M B, ci, At, u.an, ei. au. M, R, 01, AI, AO, Otf M, at, at, K M-10, M, MOOI At, AO, It BX, DI, AS, At, AO, »1, M, It OarU.ttefHi At, Γ
	А мт мб tfw- tfw- 15>w- и– и– 15500- 15500-		но inf CLATEROE R44909B CLATEROE CLATE	auw-cin >TP- IMTR IIII IMTR IIIII IIIII IIIII IIIII IIIII IIIII IIII	M, 01, 14, At, At, oto H, ás, AI, 010 M-SL: M STL (XAV SIA
	A MT Mo*« Mi—- tro- trw- 15»w- w 15500- 150 150 150 150 150 150 150 150		но inf CLAYRORE CLAYRONE CLAY	auw-ciii >TP- IMTR IMTR IUw-Bi IUw-Bi IUw-Bi Muro- Iuw-Bi Bi Or > M IUW-D III IUW-Bi III IUW-Bi III IUW-Bi III III III III III III III III III I	N, 01, 14, At, At, oto H, ās, Al, 010 M, st, Al, 010 M, st, Al, 010 M, st, Al, 301, At, At, 31 BI, 01, 04, AI, AO, M, »f, M, M, M, ote, oummen, oio C. Gi. GIT. AI. At, At, 31 te aheve u otaw M-01, 05, At, Ai, >1, oto Nojí i> iA AL, AL, AL, AL, AL, AL U DI LITAS M, AT, AJ N, 01, OI, S, At, Ai, >1, oto Nojí i> iA, AL, AO, M B, Ci. At, u.an. ei. au. M. R, 01, AI, AO, Otf M, at, at, K OoM, MMOOI At, AO, It SXIn fia AH MIT oarU. ttefHi At, Γ
	A MT Mo*« Mf trw- 15»w- U W 15500- 1500-A W- MO*-' UI		но inf CLAYBOOR CLAY	auw-cini >TP- Tr-St. IMTR IUw-Bi IUw-Bi Muro- IUw-Bi Al- Mw- Iumai niwo- States Iumai niwo- States Iumai niwo- States Iumai niwo- States Iumai I	N, 01, 14, At, At, oto H, ás, Al, 010 M-51 = M STL (ЖАУ ЗКА BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), oio CL 01, 05, At, AI, AL, AL, AL, AL te aheve u otaw M-01, 05, At, Ai, >1, oto N01 { 101 AJ, AL, AL, AL, AL, AL N, 01, 01, >1, AI, AO, M s, ci, At, u.an, ei, au, M, R, 01, AI, AO, Otf M, at, at, K South Sack Concellent, AL, AL, AL N, 05, AS, At, AO, »1, M, It Sach The Hi MIT
	A MT Mo*« HO'- ttw- 15»ν- IU W 15500- 150 Λ MO'- UI-		KANNER KANNER	auw-cin >TP- IMTR III	M, 01, 14, At, At, oto H, ás, AI, 010 M-51, M STL (ж. A) StA BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), oio C. 61, 617, AI, A2, A5, 31 te aheve u otaw M-01, 05, At, Ai, >1, oto Noj [] [] [] [] [] [] [] [] [] [
	A MT Mo*« Mf tfW- 15>w- IU W 15500- 150 N W- 15500- UI		но inf CLAYPOOR CLAY	auw-cini >TP- im g. imTR imTR imTR imtwo- imto- imto- imto- imtwo- imtwo- imto-	M, 01, 14, At, At, oto H, ás, AT, 010 M-SL: M STL (ЖАУ ЗКА BI, 01, 04, AI, AO, M, »f, M, M, M, ote, оцимиви), olo C. SL: CI. AL, AL, AS, M te aheve u otaw M-01, 05, At, Ai, >1, oto NOI (I) (I) (I) (I) (I) (I) (I) (I) (I) (I
	A MT Mo*« Mf—- tfor- tfw- 15>w- IU W 15500- 150 150 150 NO*-' UI'-		AARDERE	auw-ciii · · · · · · · · · · · · · · · · · ·	N, 01, 14, At, At, oto H, ās, Al, 010 M, st, Al, 010 M, st, Al, 010 M, st, Al, AD, M, »f, M, M, M, ote, oummen, oio C. 61. 617. Al. Al. Al. Al. 11 te aheve u otaw M-01, 05, At, Ai, >1, oto Noj []] [] [] [] [] [] [] [] []
	A MT HO*- HV- 15500- 150 MO*-' U'- NO*-' U'-		но inf CLAYBOOR R449098 CLAYBOOR CLAYB	auw-ciii >TP- IMTR III IMTR IIIW-Bi IIIW-Bi IIW-BI IIW-BI	N, 01, 14, At, At, oto H, ás, Al, 010 M-51 = M STL (ЖАУ SVA

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