

ELECTRON-OPTICAL STUDY OF ALTERATION TO SMECTITE IN THE CHETO CLAY DEPOSIT

by

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ABSTRACT

VOLCANIC ash of latitic composition in the Pliocene Bidahochi formation of northeastern Arizona has been altered in place to smectite clay. The Cheto clay, a 4-ft thick bed of high-quality activable smectite, offers an excellent opportunity for electron-optical study of the alteration processes in volcanic glass shards, spherulites, and aggregates in the tuff. No completely unaltered tuff remains in the exposed bed, but transitional materials showing progressive alteration from vitric tuff toward massive smectite have been collected and examined petrographically, electron-optically, and by X-ray diffraction.

The partly altered tuff shows several clearly identified structures relatable to the fresh material: spherical to subspherical spherulites, conchoidally fractured subtriangular to irregular vitric shards dominated by smoothly curved pitted surfaces, massive essentially structureless glass, and columnar fused aggregates which appear interstitial to the shards. Upon alteration these aggregates display an irregular comb-like structure from a planar base in cross-section, and a hackly polygonal to random texture normal to the comb structures. X-ray diffraction reveals only montmorillonite in the materials examined, although minor quartz and plagioclase feldspar have been reported elsewhere in the partially altered ash.

Argillization of the vitric tuff involves several phenomena: (1) the development of layering or banding in the glass; (2) the development of a braided surface aspect perhaps related to banding; (3) the inception of arcuate subparallel lineations on internal curved surfaces of the glass; (4) the growth of pseudo-hexagonal, weakly curled flakes whose boundaries appear threadlike on glass surfaces, and (5) the growth of grossly hexagonal matted granular networks in completely altered glass. Bladed, comb-like smectite develops along interfaces between glass and more resistant shards and from fused columnar aggregates in the original material. The mechanism appears to be one of essentially pervasive nucleation and growth of smectite in the devitrifying glass with the early development of preferred orientation of individual smectite crystallites. This orientation, manifested in layering and braiding, may reflect simple response to the space problem or response to cryptostructures and polymerization in the original glass. Relic structures relatable to the unaltered vitric tuff are not obliterated and can be discerned even in the completely altered ash.

INTRODUCTION

THE Cheto clay deposit is a stratum of low-swelling smectite derived by the weathering of a vitric volcanic latite ash. Most of the mined clay is completely altered to montmorillonite, but some marginal portions of the deposit are

known to be incompletely altered. Ultra-microstructures developed during the alteration should be visible in the electron microscope, but a search of the literature reveals that no such pertinent study in the Cheto clays or elsewhere has been published. This investigation was made to describe and identify whatever relic structures and stages of the alteration might be discernible with the electron microscope. It is anticipated that such studies might profitably be extended to the examination and understanding of more general alteration processes.

GEOLOGIC SETTING

The Cheto clay stratum of the Pliocene Bidahochi formation is an important commercial source of activable smectite. The deposits are located in north-eastern Arizona, a few miles east and southeast of the town of Sanders, Navajo County, Arizona, which lies between Holbrook, Arizona, and Gallup, New Mexico. Current production and available samples are from the Gurley and Alba pits, readily accessible by road and 5 miles east of the Sanders Interstate Highway exit. Most of the pits indicated on published maps are totally stripped of clay and defunct.

The non-marine Bidahochi formation unconformably overlies Triassic and older sediments on the southwest flank of the Defiance Plateau (Kiersch and Keller, 1955). The formation has been divided into three units by Repenning and Irwin (1954), the local equivalent of the middle unit of which is important here. In the area of the pits examined, it consists of latitic ash, now altered to smectite, deposited in clean disconformity upon underlying poorly-indurated lacustrine siltstones and sandy mudstones of the lower member. The lower surface is locally stream-channeled. The clay horizon is not uniformly continuous and of even thickness but rather is locally stream-channel scoured, thickened and thinned by mass movement, and depositionally pinched out. The upper member of the Bidahochi formation consists of friable to loose fluvial sands, silts, and muds. This overburden, which is removed in mining the clay, varies in the pit area from a few to 75 ft in thickness. The reader is referred to Kiersch and Keller (1955) for maps, cross-section and fence diagrams, and much more complete information than is appropriate here on geologic setting, lithology, and stratigraphy of the Bidahochi formation.

The source of the original ash is not specifically known. Volcanic activity was widespread in Arizona and New Mexico during Pliocene time, and air-borne ash was probably deposited over thousands of square miles from tens or hundreds of vents.

The clays are light beige, flecked sparsely with black manganese oxides, except for a 6 in. thick pinkish layer within 6 in. of the bottom. The clay when moist breaks conchoidally and has a slippery texture. When dried it becomes snow white, first fracturing and then virtually granulating as it dehydrates.

The ash stratum in the Gurley and Alba pit area is found to be extensively altered. Many specimens were collected but none were fresh enough to permit realistic appraisal of the composition of the unaltered ash. Analyses and diffraction traces of material from elsewhere in the area (Kiersch and Keller, 1955) show the fresh material to be X-ray amorphous, with only a broad hump from 20 to 35 degrees 2θ . Not even quartz lines are detectable. Chemical analyses by Nutting (1943) given in Table 1 of Kiersch and Keller (1955) show its composition to be consistent with that of latite. The fresh material therefore appears to have been a vitric latite tuff.

The altered clay is a calcium montmorillonite, an identification supported by its color, its physical properties (particularly its low swelling characteristics), and its X-ray diffraction pattern.

INVESTIGATION

The site of current strip-mining operations of the Cheto clay was visited by the authors to secure samples of the clay for study. At present, operations are being carried on in two pits, the Alba Mining Company pit and the Gurley pit immediately northwest of the Alba pit. Most of the samples used in this study were secured from the northwest part of the Gurley pit.

Approximate 2-lb samples were taken through a vertical 4-ft section at the following depths: about 3 in. below the top of the seam, 2 ft below the top, 3.5 ft below the top, and through the bottom 6 in. It should be noted that, at both pits, the bottom 6 in. represents a stratum distinct from the conformably overlying 3.5 ft of clay. Two samples of incompletely altered material were taken from the Alba pit dump. Presumably, the dump material had come from the pit margins.

Field samples were thoroughly air-dried in the laboratory for a period of several weeks. After air-drying, representative portions of each of the field samples were fractured carefully to produce fresh, reasonably smooth fracture surfaces for replication. Debris from the fracturing was gently blown free of the fracture surfaces and the specimens were placed in a vacuum desiccator for drying. When thoroughly vacuum-dried, fracture surfaces in the specimens were replicated in a thin-film vacuum evaporator. Direct platinum-shadowed carbon replicas were made of fracture surface areas approximately 6 mm square.

Carbon replicas were reinforced by the polystyrene disc method described by Bates and Comer (1955) and were freed from the specimens by immersion in distilled water or in concentrated hydrofluoric acid. Clay particles were removed from the reinforced replicas by floating in alternate baths of concentrated hydrofluoric acid and 0.5N sodium hydroxide until clean. Replicas were scored into approximate 2 mm squares and freed from the polystyrene reinforcement as described by Bates and Comer (1955). Replica squares were cleaned of polystyrene in several baths of ethylene dichloride before being picked up on standard 3 mm diameter, 300 mesh copper support grids.

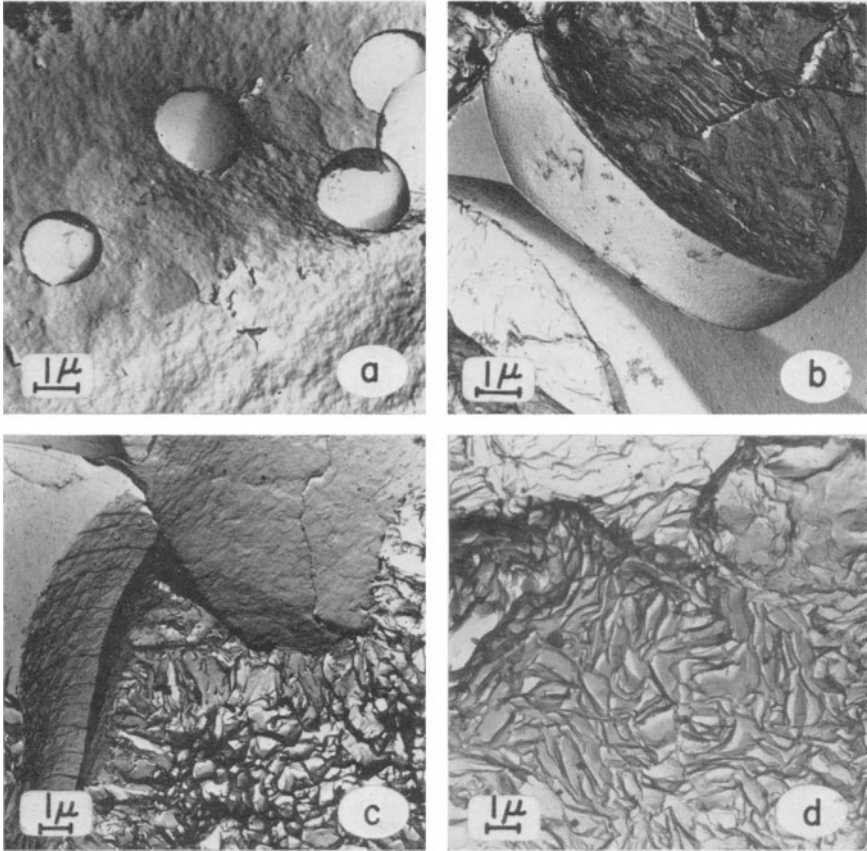


PLATE 1

Replica specimens were scanned in an Hitachi HS-7 electron microscope at approximately 5000 diameters magnification and 50 kV accelerating voltage. Representative areas and specific morphological features in each replica were recorded photographically on $3\frac{1}{4} \times 4$ in. glass plates.

RESULTS

Salient structural features in the freshest material available, from discarded material near the fringes of the Alba pit, include the spherulites of micrograph *a*, Plate 1, and the arcuate to subtriangular vitric shards of micrographs *1b* and *1c*. The spherulites of micrograph *1a* occur in a massive structureless matrix of presumably glassy material which shows only sparse, random, and fine flecks of smectite. The spheroids show no detectable surficial

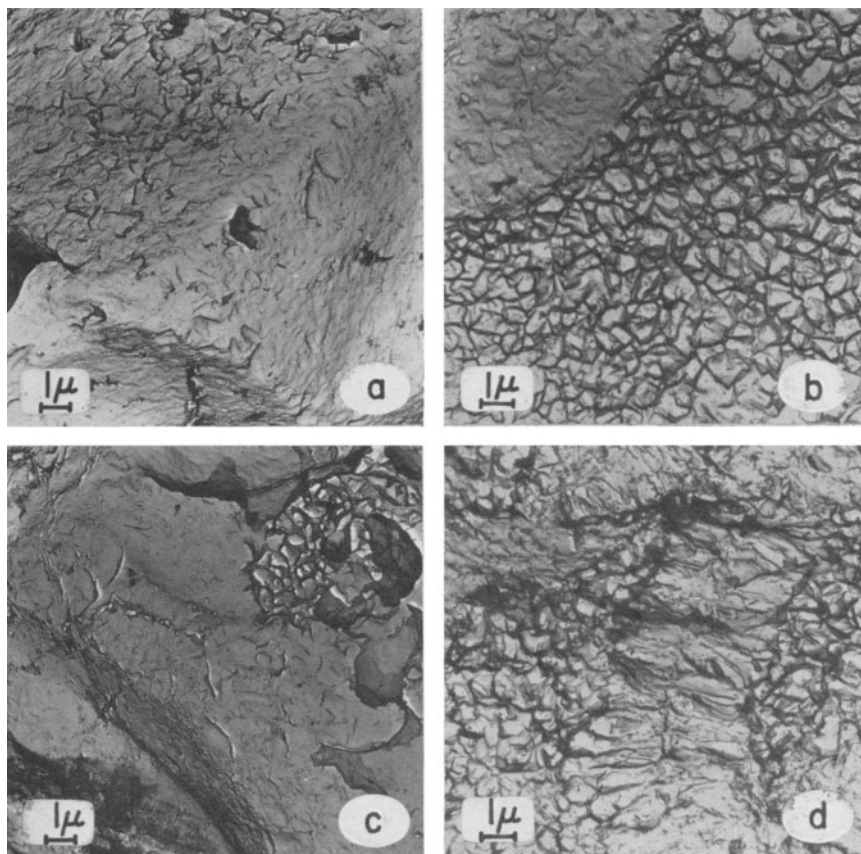


PLATE 2

alteration, and probably represent a glass of slightly different composition than the matrix, having been formed as droplets in the volcanic processes which produced the ash. The surface of the matrix material is finely pitted and irregular, showing none of the geometric features noted in more completely argillized ash. The arcuate vitric fragments of micrograph 1*b* represent fused or coalesced droplets which, like those in micrograph 1*a*, show no apparent surficial alteration, although internal incipient alteration is apparent. The light and dark lineations evident on the broken surface of the upper spherulite in micrograph 1*b* are not smooth, systematic, or continuous enough to represent subconchoidal fracture or flow lines in the glassy spherulite, and are taken to represent the development of crude layering or banding in the glass, probably the result of the first nucleation of smectite. That such

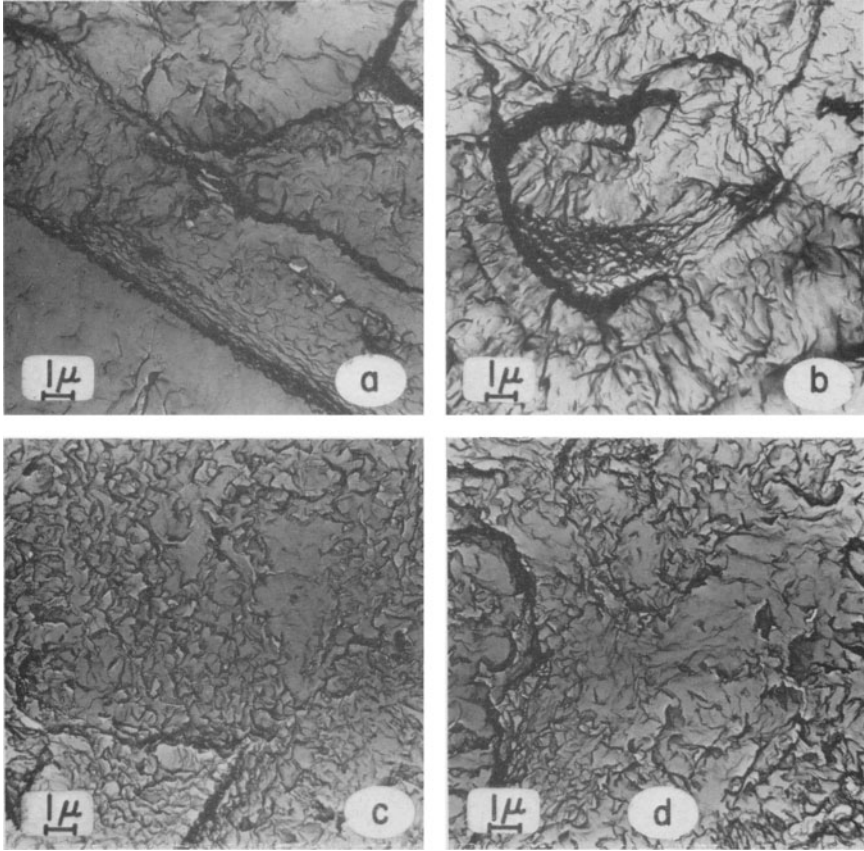


PLATE 3

nucleation has occurred is also suggested by the weakly braided, slightly ropy aspect of the remainder of the broken surface visible in micrograph 1*b*. The vitric shard is embedded in more-advancedly argillized material visible at the upper and lower left corners. The shards of micrograph 1*c* also show a ropy appearance indicating pervasive nucleation of clay mineral, again in glassy fragments which show pitted, essentially fresh-appearing outer surfaces as yet undisturbed by the internal incipient argillization. The origin of the arcuate fractures on the curved surface of the left edge of micrograph 1*c* may also reflect argillization. At first inspection they resemble conchoidal fractures developed mechanically by breakage. They seem, however, to be less regular than mechanical fractures might be and have no apparent depth. Their relationship to argillization is not clear, but they may be related to it.

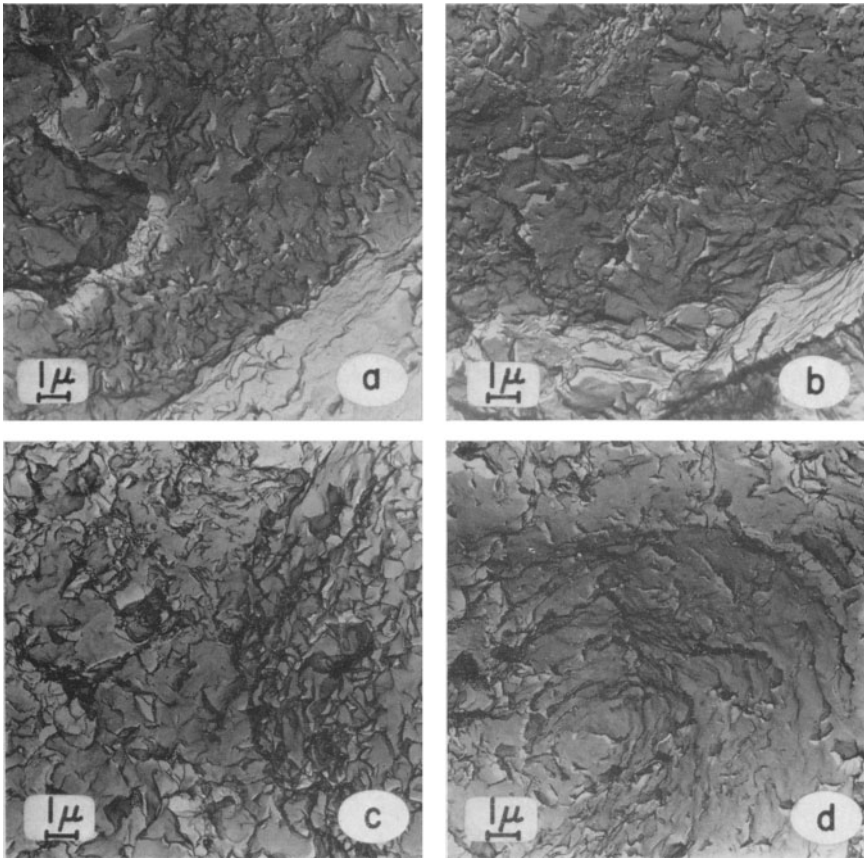


PLATE 4

Such fractures were not observed in morphologically similar shards in fresher material.

A persistent morphological feature of altered materials from both the Gurley and the Alba pits is visible in the lower right corner of micrograph 1c. Bladed montmorillonite units aligned normal to less-altered vitric shards yield outwardly to compact, more equigranular, sub-polygonal to irregular units, a phenomenon to be more fully discussed below.

Micrograph 1d shows another specimen collected in the fresher marginal material at the Alba pit. Its "grain of wheat" texture is unlike any seen in more pervasively altered glass. No pseudotrigonal, pseudohexagonal, or even systematic polygonal symmetry is apparent; rather it resembles an advanced state of the ropy, braided incipient argillization evident in micrograph 1b.

Little can be concluded from it save that it probably represents an early phase of glass argillization.

Micrographs *a*, *b*, and *c*, Plate 2, all represent early stages in the alteration history, and all are from specimens collected in the fresher material. Micrograph *2a* shows several phenomena developed in material morphologically grossly similar to the flatter shard areas in micrograph *1b*. Surface checking, showing predominantly pseudo-hexagonal intersections, has developed relatively sparsely in the plane of the dominant surface near the top of the micrograph. Some minor flakes have curled up slightly from the surface. That this pseudo-hexagonal curling is planar in extent is indicated by the lamination, parallel to the principal surface, evident on the steep face near the bottom of the micrograph. Development of smectite appears, then, to have proceeded along layers, or bands, in the glassy matrix. These same features are evident in micrograph *2c* which shows sub-polygonal to pseudo-hexagonal growth of smectite with attendant curling and with strong evidence for laminar development in the "cross-section" views on the steep surfaces at the upper left and lower center. Note also the featureless apparently unaltered material at the top of this micrograph which resembles the unaffected areas of micrographs *1a* and *2a*.

Micrographs *b* and *d*, Plate 2, have been selected to show different but related features of progressive development of smectite in more altered material. Micrograph *2b* shows a large area of granular, matted smectite in the lower right of the micrograph which may have developed from the curled flakes of micrographs *2a* and *2c*. Pseudo-hexagonal boundaries are evident, but they have been subdued by a more pervasive, heterogeneous, and massive growth of montmorillonite.

The bladed columnar aggregates of micrograph *2d* (and of micrograph *1c*) deserve special attention in view of their singular appearance. They might be taken to represent either the "earliest" formed montmorillonite lining cavities and vapor phase vesicles in the primary glass, or locally transported smectite grown outward in altering glass from fractures and discontinuities within it. Micrograph *2d*, which shows bilateral symmetry of the bladed material, is atypical, the simpler symmetry of micrograph *1c* being the more common occurrence. In view of the rarity of the bilateral type, it is thought that these bladed comb-like aggregates reflect a relic structure in the glass, probably fused glass and columnar aggregates adjacent to shards, lining vesicles, and as septa between vesicles. It can also be shown tentatively that a view normal to one of these comb-like structures reveals a random to hackly polygonal structure not unlike that of micrograph *2b*. These comb-like structures are interpreted to be relic structures reflecting growth of bladed-columnar smectite from discontinuities between shards and vitric tuff and from fractures in glass which yield to the more compact massive granular material.

Plates 3 and 4 show pairs of photographs of samples collected at various depths in the 4.0 ft thick Cheto clay horizon at the Gurley pit. The material

is all completely argillized. No recognizable shards remain in the clay matrix. Although all of the specimens are more completely altered than those from the Alba margin, the uppermost ones are less pervasively affected than the lower ones. Micrographs *3a* and *3b* are specimens 3 in. from the top, micrographs *3c* and *3d* 2 ft from the top, micrographs *4a* and *4b* 3.5 ft from the top (the pink layer previously described), and micrographs *4c* and *4d* are from specimens taken 1 in. from the bottom (3.9 ft from the upper surface). The pairs are selected to show relatively orthogonal relic structures on the left and relatively arcuate ones on the right.

Micrograph *3a* shows both orthogonal and arcuate structures in material which exhibits strong development of the layered or laminated structure in the NW-SE band across the center of the figure, with the curling structures on the upper surface. The subcircular structure at the top may represent an altered spheroid as in micrograph *1a*. The relatively clear field at the lower left shows no external apparent well-developed argillation, although it may be present internally. Micrograph *3b* shows an entire field of the comb-like material roughly radial to a central incomplete arcuate structure. The crudely triangular patch just below center suggests the random-hackly appearance of a view normal to the comb-like altered fused columnar structures.

Micrographs *3c* and *3d* both show smectite structures indicating end-point advancement of the curled flaky structures of micrographs *2a* and *2c*. The principal surface is uniformly affected with matted, heterogeneously-oriented flakes and grains of smectite. A few pseudo-hexagonal incipient flakes are visible in micrograph *3d*, but the most obvious structures in both micrographs *3c* and *3d* are relics of the shard-matrix material of the original vitric tuff.

Micrographs *4a* and *4d* require little comment. Primary interfaces and columnar aggregate structures are nearly obliterated in a felted massive smectite. Micrograph *4c*, for example, shows pervasive argillization with no areas suggesting either prominent primary structures or the persistence of glass remnants. Micrograph *4d* shows an arcuate structure which may be a remnant inherited from the original alteration in the fresh tuff.

CONCLUSIONS

Several significant conclusions result from this initial morphological study of alteration to smectite of a completely vitric latitic tuff. Inception of alteration is not uniform throughout the specimens, but, as might be expected, first attacks the more susceptible glassy phases. More resistant phases, the shards of Plate 1, indicate that argillization develops fairly spontaneously throughout a given shard to produce a layered or braided appearance on internal surfaces with external bounding surfaces apparently unaffected. Continued alteration intensifies the layering and produces pseudo-hexagonal ruptures on the outer surfaces which appear to be slightly curled plates. Lamination is strongly developed in the planes of these platy crystallites.

More advanced alteration, concurrently in the more susceptible matrix, takes the form of granular compact masses limited toward shards by comb-like bladed aggregates. Blades of these aggregates are normal to interfaces between two primary glass phases and along what appear to have been columnar fused aggregates in the unaltered material. These comb-like aggregates show a polygonal-granular aspect in cross-section not unlike the granular compact masses grown in the massive glass. Perhaps most significant is the fact that structures relatable to the unaltered tuff are still discernible in the most completely altered material examined.

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