

RESILICATION OF BAUXITE AT THE ALABAMA STREET MINE, SALINE COUNTY, ARKANSAS, ILLUSTRATED BY SCANNING ELECTRON MICROGRAPHS

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Abstract—Resilication of bauxite produced kaolin at and beneath an old erosion surface on bauxite at the Alabama Street Mine of ALCOA in Saline County, Arkansas. The transitional alteration can be traced in morphology by scanning electron microscopy, (SEM) and in Al:Si ratio by energy dispersive analysis. In one illustrated example, the sequence of resilication took place within 1 mm thickness; in another, across 80 mm. The first morphologic alteration of gibbsite (bauxite) appears to be to allophane that occurs in micrometer-size plates which show elongate cracking and/or straight to highly curved elongate edges. The next phase is kaolinite, first in micrometer-size flakes followed by coarser flakes that grade into a zone of typical stacked kaolinite, likewise identified by X-ray powder diffraction. Notably large stacks and small flakes of kaolinite are intimately mixed in the SEMs, thus suggesting that unequal sizes of kaolinite crystals can grow during one episode of an in-situ genesis.

Key Words—Allophane, Al:Si ratio, Bauxite, Gibbsite, Kaolinite, Resilication, Scanning electron microscopy.

INTRODUCTION

Kaolinite occurs in the bauxite deposits of Arkansas in a variety of relationships, such as in layers above or below the bauxite, as vein fillings, as replacements, and with either gradational or relatively sharp contacts with bauxite or nepheline syenite. The purpose of this paper is to show by scanning electron micrographs (SEM), augmented by energy dispersive analyses (EDX), stages in the resilication of bauxite to kaolinite in two specimens collected from a representative commercial deposit of bauxite in Arkansas. In one sample kaolinization took place within 1 mm, whereas in the other, it extended across 80 mm.

FIELD OCCURRENCE AND LITHOLOGY

Hand specimens containing both bauxite and kaolinite in contact were collected from the Alabama Street Mine, courtesy of ALCOA, in the NE¹/₄ SW¹/₄ Sec. 15, T2S, R14W, Saline County, Arkansas. This bauxite ore is of the conglomerate type (Gordon *et al.*, 1958) that subsequently, in Eocene time, had been eroded to a bouldery upper surface and then overlain by a carbonaceous sand. A hand specimen broken from the top of the ore body shows (Figure 1) the smoothed, kaolinized, upper surface and the underlying rougher pisolitic nature of the conglomerate ore.

The gibbsite in the bauxite, and the kaolinite in the surface layer, were identified by X-ray powder diffraction (Figures 2a and 2b). Their microtextures are shown in Figures 3 and 4, in which the texture of the bauxite is typical of the lateritic variety (Bárdossy *et al.*, 1978; Keller, 1979), and the texture of the kaolin is similar

to that of kaolinite from Georgia or Cornwall (Keller, 1978).

EXPERIMENTAL

For scanning electron micrography, small chips were broken from the hand specimens to expose fresh surfaces which were examined without further processing than to coat them with a thin layer of gold to carry away excess charge from the electron beam. An essentially continuous sequence of chips was taken across the specimens at changes in morphology from the bauxite to kaolinite.

Energy dispersive analyses were made either over an entire area in a micrograph or on selected spots and reported as Al:Si ratios. The ratio-estimating analytical technique is quite suitable for this study because Al and Si (with accessory Ti) are the distinguishing constituent elements, apart from O and H, in both gibbsite and kaolinite. Moreover, because ratios rather than absolute values are obtained, determinations may be made on the naturally inclined (to the electron beam) cleavage surfaces of mineral grains because the inclination is the same for both elements.

Si is reported about 10% high in the ratio because of minor absorption of Al by Be in the detector. For example, kaolinite ideally should show an Al:Si atom ratio of 1:1, but independently analyzed reference specimens typically yield ratios of 1:1.1. Pure gibbsite ideally should show Al:Si as 1:0.0, but bauxite, which commonly contains trace amounts of kaolinite, typically yields a number in the second decimal place, as 1:0.0x. However, because the main objective of the EDX analyses was to estimate the relative amounts of

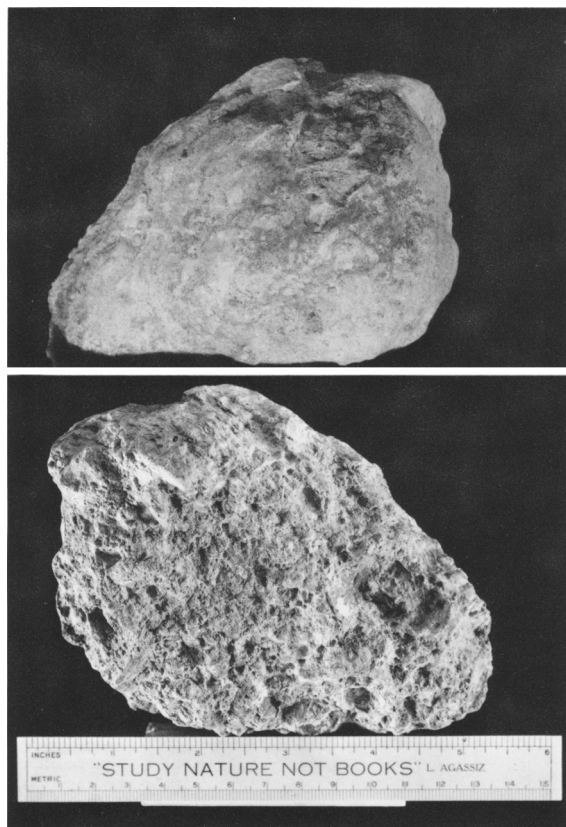


Figure 1. Hand specimen 1 from Alabama Street Mine (ALCOA), Saline County, Arkansas. Upper photo shows the smoother, kaolinized surface of the bauxite at an old erosion surface. Lower photo shows the rougher, pisolitic surface of the same specimen as broken from the bauxite beneath.

gibbsite and kaolinite in the areas examined, comparative Al:Si ratios by the EDX spectra satisfactorily furnish this information. More than 100 SEMs and 150 EDX analyses were made from the two hand specimens described in this report.

TRANSITIONAL STAGES OF RESILICATION SHOWN BY SCANNING ELECTRON MICROGRAPHY

Hand specimen 1

A single chip from the hand specimen shown in Figure 1 displayed a full progressive sequence from gibbsite to kaolinite, presumably because the fracture fortuitously took place along an inclined, stepwise surface across the transition (Figure 5). The microporous material at position A in Figure 5 that extends to the lower part of the micrograph is shown in Figure 6. Its morphology is that of bauxite (gibbsite), and its Al:Si ratio is 1:0.09 for the picture area, confirming its identification as gibbsite. In the upper right-hand corner, how-

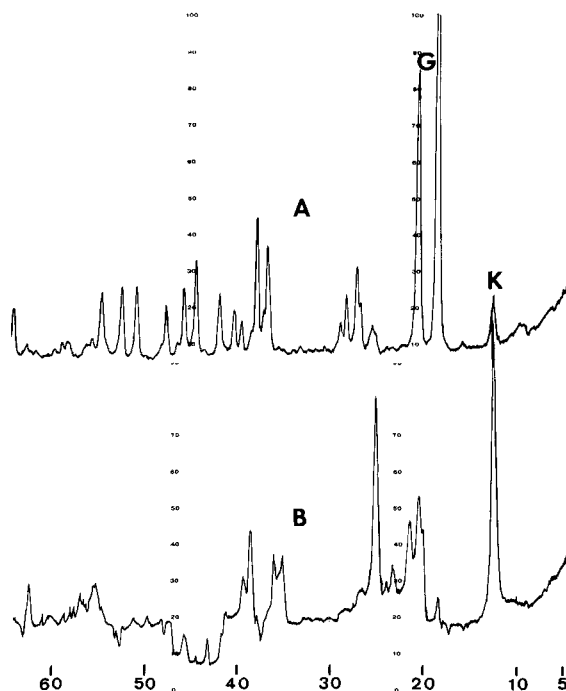


Figure 2. X-ray powder diffractograms of (A) gibbsite from specimen 1 and of (B) kaolinite from specimen 2. Strong reflections of gibbsite are indicated by "G," and of kaolinite by "K." CuK α radiation. Degrees 2θ along base.

ever, of Figure 6, above spot 1, are several different crystals or grains that are elongate in cross section, suggesting a change in morphology. They increase in amount toward position B in Figure 5. This area is magnified in Figure 7 in which the band of elongate shapes crosses it diagonally above spot 1. These elongate forms are variously straight, curled, or "Y"-shaped bifurcated edges of plates, more clearly shown at higher magnification in Figures 8 and 9. Their Al:Si ratios are 1:0.09 at spot 1 in Figures 6 and 7 (same location) and at spot 1 in Figure 8. Additional analyses of similar structures in other SEMs not shown yielded ratios of 1:0.09, 0.10, and 0.12. On the basis of their variable composition, platy structure, and mineral association, these particles are likely allophane, probably alumina-rich allophane. Thus, the allophane occurs as if it had originated from parent gibbsite to which variable amounts of silica had been added.

The allophane shapes decrease gradationally upward to another zone, such as occupies the upper part of Figure 7, likewise at position C on Figure 5, and also separately shown in Figure 10. The Al:Si ratio of the area in Figure 10 is 1:0.24 which represents a significant increase in Si from that in Figures 7 and 8. It is inferred that the tiny stacks in Figure 10 represent kaolinite that developed from grains of gibbsite.

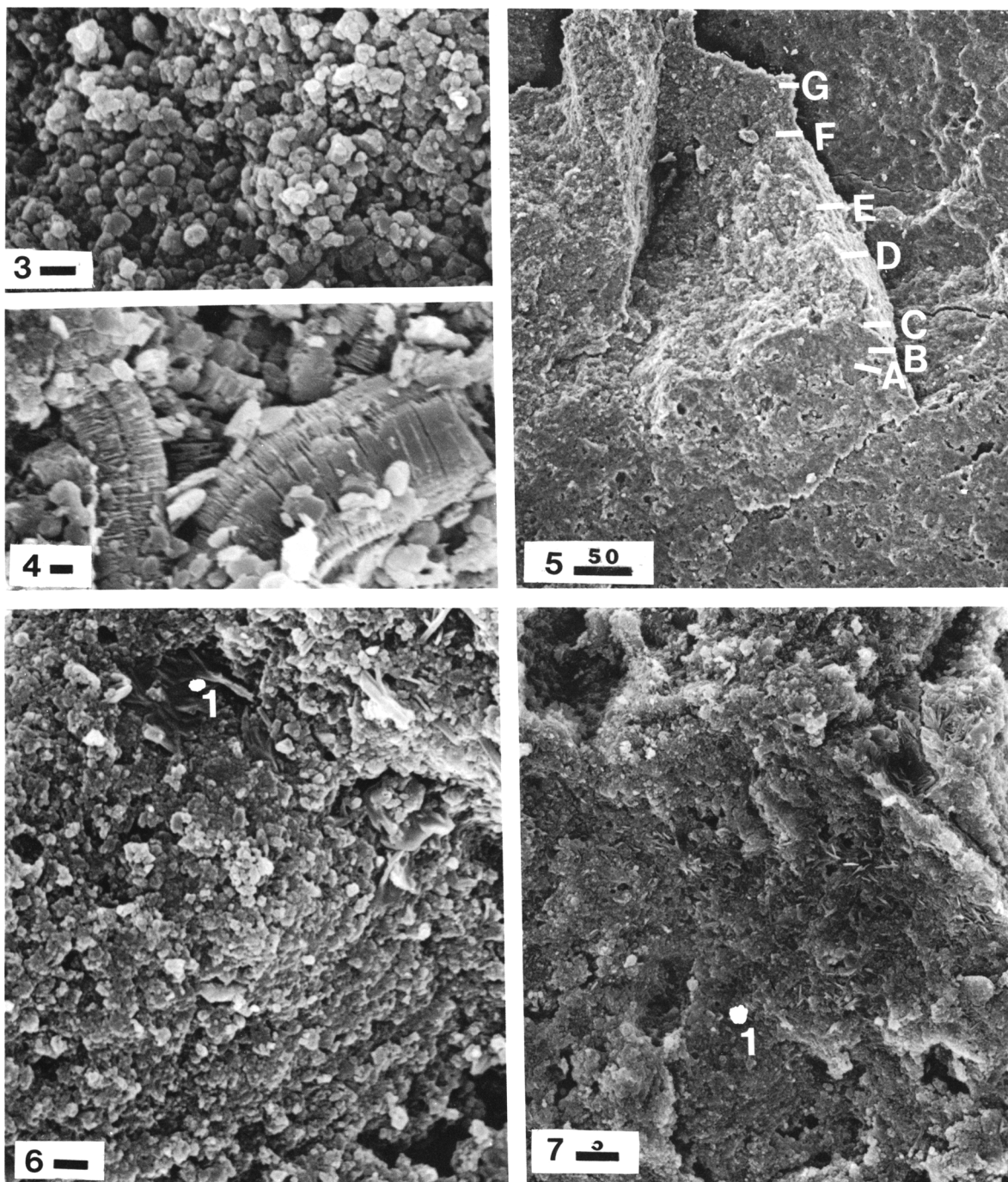


Figure 3. Scanning electron micrograph of the gibbsite from the lower pisolitic bauxite in Figure 1. Bar = 1 μm .

Figure 4. Scanning electron micrograph of kaolinite from the upper surface of the kaolinized bauxite in Figure 1. Bar = 1 μm .

Figure 5. Scanning electron micrograph of an inclined fracture surface across a representative chip broken from the kaolinized upper surface of hand specimen 1 (upper photograph in Figure 1). Bar = 50 μm .

Figure 6. Scanning electron micrograph of gibbsite at position A in Figure 5. A mineral transition zone begins near spot 1 and continues into the upper, right-hand corner. Bar = 1 μm .

Figure 7. Scanning electron micrograph of transition zone, composed of tiny elongate forms, that crosses the micrograph above spot 1. The zone intervenes between gibbsite below, and first-stage kaolinization above. Bar = 5 μm .

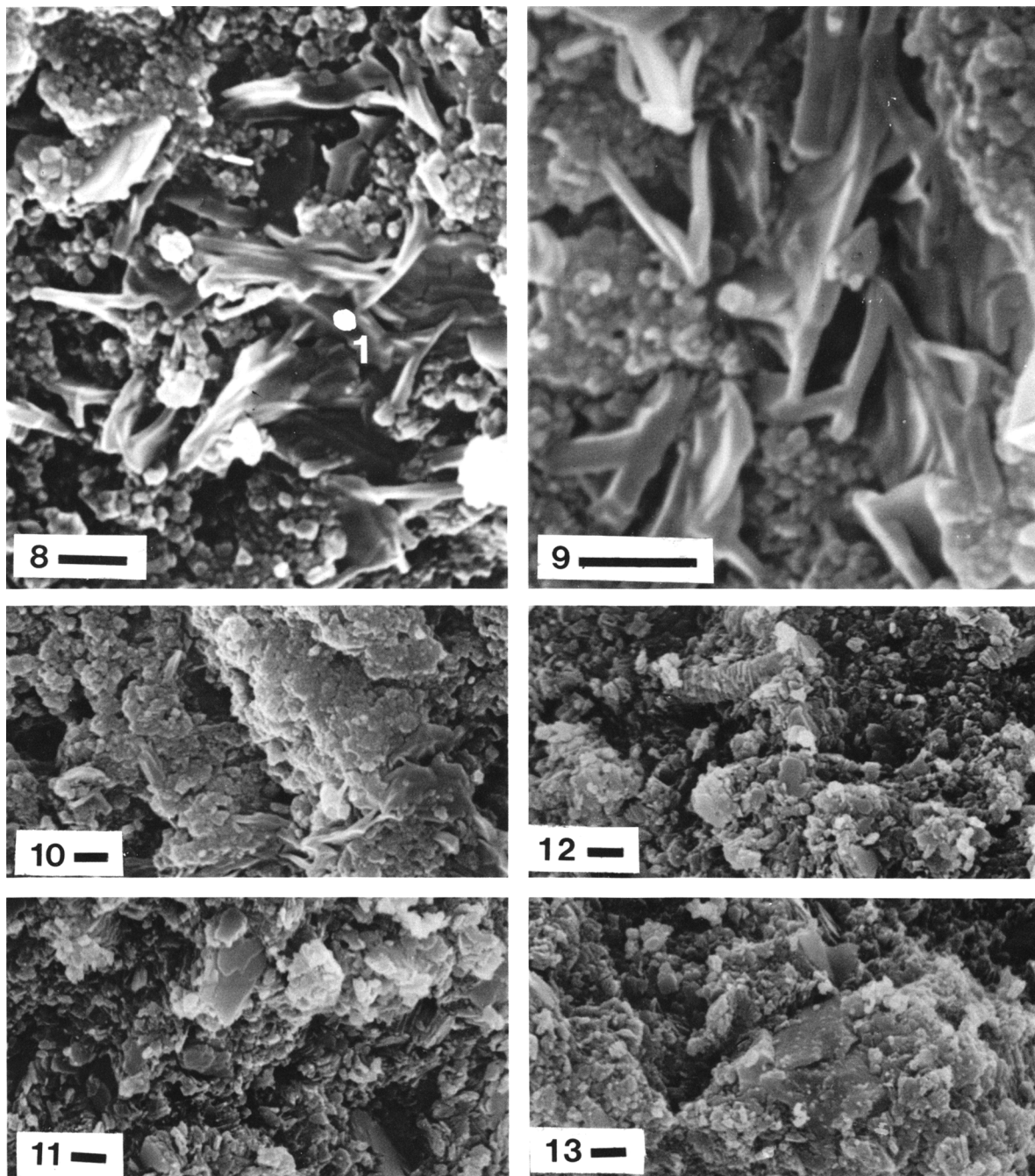


Figure 8. Scanning electron micrograph of curved edges of transitional plates(?) inferred to have formed from dissolved gibbsite with the addition of dissolved silica. Bar = 1 μm .

Figure 9. Scanning electron micrograph of transitional plates at higher magnification. Bar = 1 μm .

Figure 10. Scanning electron micrograph of plate-like particles that are interpreted to have developed from clusters of gibbsite grains. Bar = 1 μm .

Figure 11. Scanning electron micrograph showing flakes with kaolinite-type morphology in aggregates resembling former(?) gibbsite grains. Bar = 1 μm .

Figure 12. Scanning electron micrograph of tiny flakes of kaolinite. Bar = 1 μm .

Figure 13. Scanning electron micrograph of small flakes and a stack-like mass of kaolinite. Bar = 1 μm .

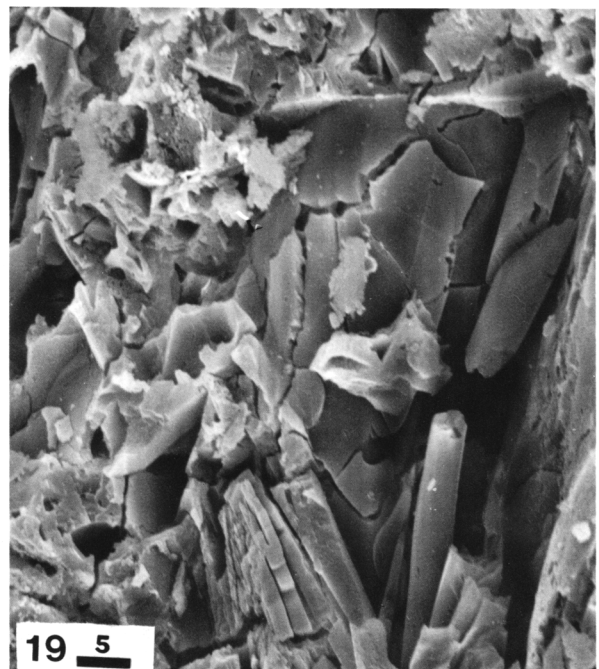
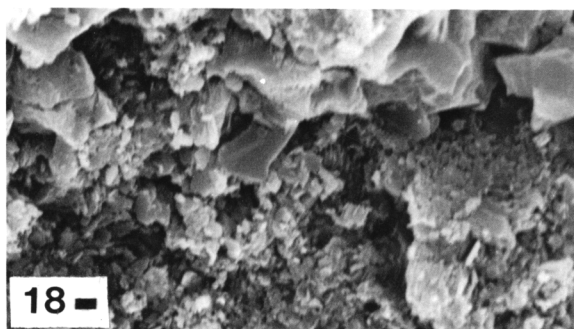
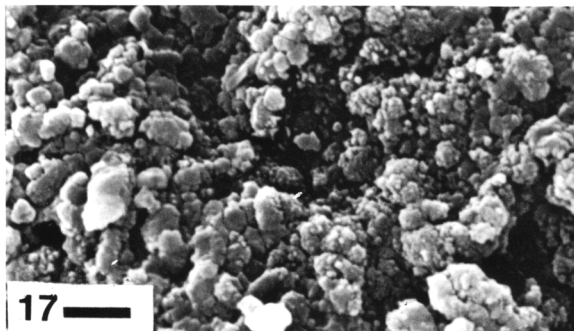
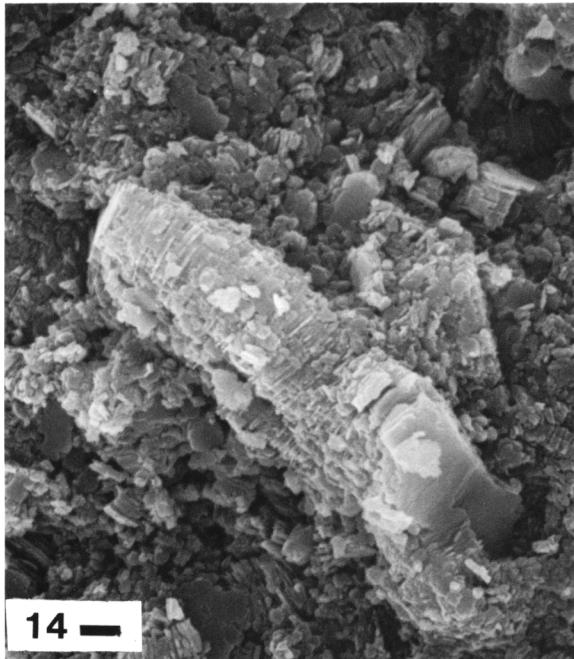


Figure 14. Scanning electron micrograph of plates and stacks of kaolinite. An Al:Si ratio of 1:0.84 indicates the presence of a small residue of unaltered gibbsite with the kaolinite. Bar = 1 μm .

Figure 15. Scanning electron micrograph of large stacks of smaller flakes of kaolinite with an Al:Si ratio of 1:1.09, indicating complete kaolinization in the lowermost layer in Figure 5. The surface shown is the underside of the top layer in the chip from the field specimen, mounted top-side down on the microscope stub. Bar = 1 μm .

Figure 17. Scanning electron micrograph of typical gibbsite. Bar = 1 μm .

Figure 18. Scanning electron micrograph showing the transition of gibbsite grains to a zone of platy morphology at the top of the micrograph. Bar = 1 μm .

Figure 19. Scanning electron micrograph of cracked plates in a transition zone between gibbsite and first-stage kaolinization. The morphology of this material resembles that of reference allophane. Bar = 1 μm .

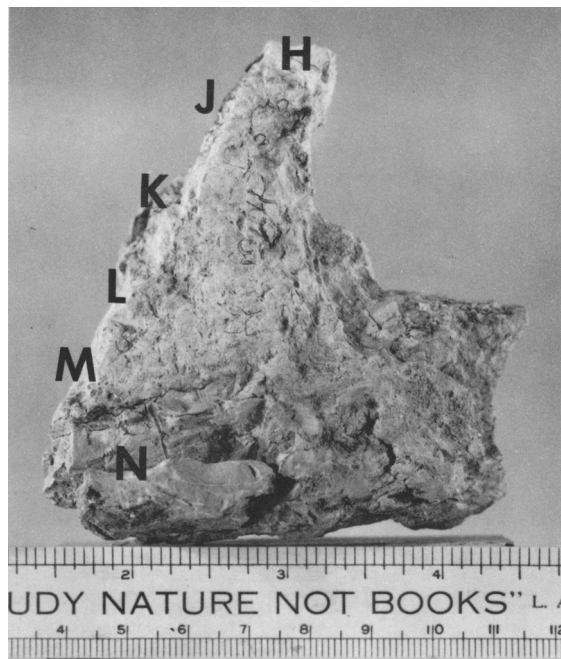


Figure 16. Hand specimen 2 in which “pure” bauxite at H grades to “pure” kaolinite at N.

The area above position C (Figure 5) on a “topographic bench” at position D, is the area shown in Figure 11. The platy morphology and decrease in texture of gibbsite presage more kaolinite. The Al:Si ratio in the entire area of Figure 11 is 1:0.53, suggesting that approximately half of the material is kaolinite.

In the next “bench” at position E in Figure 5, shown in Figure 12, the morphology is chiefly that of small stacks of kaolinite. The Al:Si ratio of this picture area is 1:0.86, confirming the increase in kaolinite. At position F (in Figure 5), shown in Figure 13, morphology characteristic of kaolinite is present, and the area has an Al:Si ratio of 1:0.84, which is comparable to that found for position E. At position G in Figure 5, the morphology as shown in Figure 14 indicates dominant kaolinite. The Al:Si ratio in this area is 1:1.05.

The basal layer of the chip, in the area to the left of positions F and G, is shown in Figure 15; it appears morphologically to be entirely kaolinite, which is supported by an Al:Si ratio of 1:1.1. Significantly, the crystals range in size from thin individual flakes less than 1 μm in diameter to flakes 10 μm in diameter stacked in books 15 μm thick. Presumably these disparate sizes formed, or “grew” by a single crystallization process that operated within a single genetic episode. In other environments, however, unequal sizes of kaolinite crystals may originate from dissimilar parent materials, by nonuniform sorting during transportation and deposition, or from multiple sources.

Hand specimen 2

In hand specimen 2 (Figure 16), the transition zone between gibbsite at H, to kaolinite at N, is 80 mm wide. At H, the texture is typical of bauxite, as shown in Figure 17, and confirmed by an Al:Si ratio of 1:0.06. The bauxite grades toward J into platy crystals (Figure 18) that fracture to elongate fragments as shown in Figure 19. The cracked material resembles in structure the naturally occurring, reference allophane illustrated in SEMs by Lahodny-Sarc *et al.* (1981). The Al:Si ratio of the area is 1:0.12. Nearby, within the same microspecimen mount, are curved and rounded forms (Figure 20) that are apparently the same material as the presumed allophane shown in Figures 8 and 9 of hand specimen 1. The Al:Si ratio at spot 1 in Figure 20 is 1:0.14, and for the entire area, 1:0.32.

The tiny, powdery particles partly covering or “dusting” the larger curved forms in Figure 20 are morphologically similar to kaolinite produced during the first stages of hydrothermal synthesis (Lahodny-Sarc *et al.*, 1978). Similarity in morphology taken alone is only suggestive of kaolinite, but the identification is strengthened by the occurrence nearby of coarser, powdery particles (Figure 21) with an Al:Si ratio 1:0.39. At K (Figure 22) the small particles rest on substrate material that resembles ragged kaolinite. Spots 1 and 2 of Figure 22 yield Al:Si ratios, respectively, of 1:0.41 and 1:0.55.

More well-developed kaolinite morphology can be seen at L (Figure 23) and at M (Figure 24), where the Al:Si ratio is 1:1.1, the normal ratio for kaolinite. At N, the kaolinite yielded the diffractogram in Figure 2. The crystals of kaolinite in hand specimen 2 also are strikingly nonuniform in size, as they are in hand specimen 1, attesting again that kaolinite can form in unequal sizes of crystals during one genetic episode.

DISCUSSION AND CONCLUSIONS

Evidence of resilication of bauxite to kaolinite at an old erosion surface on bauxite at the Alabama Street Mine in Saline County, Arkansas, is graphically presented. In one example, surveyed by SEM and EDX, the transition took place in microstages within 1 mm of vertical distance, whereas in another the change was across 80 mm. The first morphologic change where the advancing silica front invaded the bauxite was a gradational change from grainy gibbsite to a platy-structured material inferred from its morphology to be allophane. The inference is supported by the Al:Si ratio of the material being consistent with that of aluminous allophane. Rearward (the silica side) of the altering front, the platy allophane grades into tiny flakes of kaolinite. These flakes grade into a mixture of coarser flakes and large stacks of kaolinite that are typical of kaolinite deposits. This association of large kaolinite stacks set within a loosely packed matrix of smaller flakes and crystals all of which developed apparently

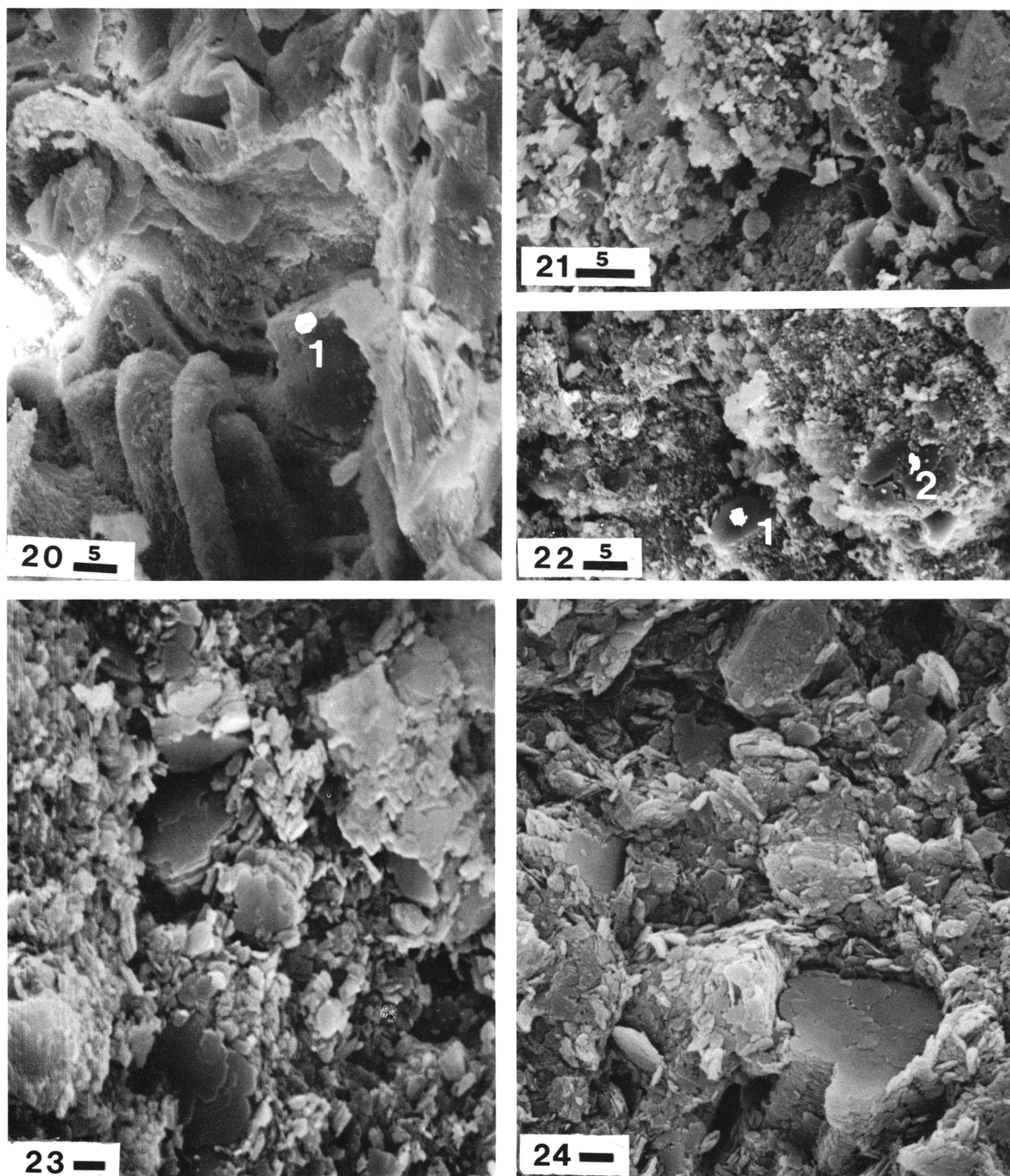


Figure 20. Scanning electron micrograph of curved and rounded plates, presumably counterparts of those in Figures 8 and 9, in a zone between gibbsite and partial kaolinization. The grainy coating is inferred to be newly developing kaolin-mineral crystals. Bar = 5 μm .

Figure 21. Scanning electron micrograph of grains inferred, because of their Al:Si ratio of 1:0.39, to be partially kaolinized. Bar = 5 μm .

Figure 22. Scanning electron micrograph of crystals in which the Al:Si ratio averages about 1:0.5, an increase in kaolinization in the series. Bar = 5 μm .

Figure 23. Scanning electron micrograph of large flakes of kaolinite forming stacks. They show uneven, angular edges characteristic of actively growing crystals. The smaller flakes possess similar edge-morphology. Bar = 1 μm .

Figure 24. Scanning electron micrograph of kaolinite morphology typical of that occurring in large commercial deposits. Bar = 1 μm .

in a single (resilication) environment suggests that highly nonuniform sizes of kaolinite crystals can form presumably during a single geologic episode of in-situ genesis.

The source of the silica added during resilication was most likely ground water from the sandstone that overlies the bauxite conglomerate, but the surface waters that eroded the bauxite exposed during an ancient, or the present, weathering cycle also may have been contributors.

ACKNOWLEDGMENTS

The SEM research was supported by National Science Foundation Grant EAR 81-19592. Clayton H. Johnson, the referees, and editor kindly aided in revising the manuscript.

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(Received 5 February 1983; accepted 16 June 1983)

Резюме—Ресиликатизация боксита создавала каолин на и ниже старой эрозионной поверхности на боксите в Шахте Алабама Стрит ALCOA в Области Салайн, Арканзас. Переходное изменение наблюдается в морфологии при помощи сканирующего электронного микроскопа (СЭМ) и в соотношении Al:Si при помощи анализа дисперсии энергии. В одном иллюстрированном случае, последовательность ресиликатизации имела место в слое толщиной 1 мм, в другом случае—в слое толщиной 80 мм. Первым морфологическим изменением гиббсита (боксита) является алофан, выступающий в виде пластинок микронного размера. В этих пластинках наблюдаются удлиненные щели и/или простые и сильно закругленные края. Следующей фазой является каолинит, начально в виде зерен микронного размера, а потом больших зерен, которые профилируют в зону типично упакованного каолинита, также обнаруженного при помощи порошковой рентгеновской дифракции. Значительно большие упаковки и малые зерна каолинита наблюдаются в месте (при помощи СЭМ), указывая на то, что кристаллы каолинита разных размеров могут формироваться во время одного эпизода образования. [E.G.]

Resümee—Resilifizierung von Bauxit führte zur Bildung von Kaolin an oder unter einer alten Erosionsoberfläche von Bauxit in der Alabama Street Mine von ALCOA im Saline County, Arkansas. Die allmähliche Umwandlung kann bei der Morphologie mittels Rasterelektronenmikroskopie (REM) und beim Al:Si-Verhältnis mittels energiedispersiver Analyse verfolgt werden. Bei einem dargestellten Beispiel fand die Abfolge der Resilifizierung innerhalb von 1 mm statt, bei einem anderen über einen Abstand von 80 mm. Die erste morphologische Umwandlung von Gibbsit (Bauxit) scheint in Allophan zu sein, der in Mikrometer-großen Tafeln auftritt, die läglige Ribildung und/oder gerade bis stark gebogene längliche Ränder aufweisen. Die nächste Phase ist Kaolinit, der zuerst in Mikrometer-großen Schuppen und dann in Form von größeren Plättchen auftritt, die in eine Zone aus typisch gestapelten Kaolinit übergehen, wie auch aus den Röntgenpulverdiffraktometeraufnahmen hervorgeht. Beachtenswert große Stapel und kleine Schuppen von Kaolinit sind in den REM-Aufnahmen eng miteinander vermischt, was darauf hindeutet, daß ungleich große Kaolinitkristalle während einer Episode einer in situ-Genese wachsen können. [U.W.]

Résumé—La resilification de bauxite a produit du kaolin à et sous une ancienne surface d'érosion à Alabama Street Mine d'ALCOA à Saline County, Arkansas. L'altération de transition peut être tracée selon la morphologie par la microscopie électronique (SEM), et selon la proportion Al:Si par analyse de dispersion d'énergie. Dans un exemple illustré, la séquence de resilification s'est passée en 1 mm d'épaisseur, dans un autre, en 80 mm. La première altération morphologique de la gibbsite (bauxite) semble être en allophane qui se trouve en plaques de taille micrométrique montrant des craquelures allongées et/ou des bords allongés droits à forts courbés. La prochaine phase est la kaolinite, d'abord en paillettes de taille micrométrique, suivie de paillettes plus épaisses qui s'étagent en une zone de kaolinite empilée typique, également identifiée par la diffraction des rayons-X. De remarquablement larges empilements et de petites paillettes de kaolinite sont intimement mélangés dans les SEM, suggérant donc que des tailles inégales de cristaux de kaolinite peuvent pousser pendant un épisode de genèse in-situ. [D.J.]