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X-RAY DIFFRACTION AND ELECTRON OPTICAL STUDIES ON SMECTITE AND α-CRISTOBALITE ASSOCIATIONS

NECIP GÜVEN and RALPH E. GRIM
University of Illinois, Department of Geology, Urbana, Illinois 61801, U.S.A.

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Abstract—Alteration products of volcanic materials from various localities in Wyoming, U.S.A., Italy, Yugoslavia and Mozambique are mainly smectites and cristobalites with small amounts of kaolinite.

Smectite and cristobalite form separate and intergrown aggregates of microcristallinity. X-ray diffraction studies show that the silica is α-cristobalite with a noticeable stacking disorder. Small aggregates of optically pure α-cristobalite, which were separated by an appropriate mixture of bromoform and carbon tetrachloride, are shown to contain a noticeable amount of smectite on Debye–Scherrer diffraction photographs for the samples from Italy and Wyoming, U.S.A.

Transmission electron micrographs and selected area electron diffraction photographs show, in addition to smectite and α-cristobalite aggregates, the presence of idiomorph single crystals of kaolinite.

INTRODUCTION

A HIGH temperature form of silica has been previously reported in bentonites by several investigators, Grüner (1940), Flörke (1955) and Novak (1967), among others. Experimentally Hemley *et al.* (1961) synthesized hydrothermally montmorillonite and cristobalite in the system Na_2O–Al_2O_3–SiO_2–H_2O at temperatures below 350°C. It seems therefore that smectites and cristobalites form an assemblage of geological significance in the alteration of volcanic materials. From the mineralogical standpoint there is an interesting relationship between the structures of these minerals. The tetrahedral sheets of smectites have been subjected to some controversy on the issue of whether the silica sheets contain inverted tetrahedra or are similar in arrangement as in micas. The crystal structure of α-cristobalite was recently refined by Dollase (1965). The structure consists of a cubic stacking sequence of tetrahedral sheets [SiO_4] where every other silica tetrahedron is inverted. In the following the results of our X-ray and electron optical investigations on smectite and α-cristobalite associations have been presented.

DESCRIPTION OF SAMPLES AND GEOLOGICAL OCCURRENCE

The samples were selected from the University of Illinois Grim's collection of clay minerals and they are described in the following with their collection numbers.

Bentonites from Italy (No. 183B, No. 336C)

These samples are from the island of Ponza off the west coast of Italy. The bentonites occur in vitreous rhyolitic tuff of a volcanic sequence that traverse a platform of Miocene siliceous limestone. The origin of the bentonite is not clear but probably it is the result of hydrothermal alteration with some superimposed weathering.

Bentonite from Yugoslavia (No. 302)

This sample is an altered volcanic ash in a sequence of Middle Tertiary sediments, (Karamata, 1956).

Bentonite from Mozambique (No. 468)

The bentonite occurs in a volcanic sequence near the top of the Stormberg series of the Karoo system of Liassic age. A perlitic lava overlies sandstone and dips 10–20° to the east. The perlite is altered to bentonite with extreme irregularity. At some places the alteration is complete whereas at others the bentonite is scattered through the glass, at still other places there are bentonite nodules within the perlite. The formation of the bentonite appears to be the result of hydrothermal alteration, perhaps at least in part due to reactions of gasses and vapours eminated from the lava itself as a kind of deuteric process.

Bentonite from Crook County, Wyoming (No. 516)

The sample is from the Clay Spur bed in the uppermost part of the Mowry shale of Lower

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Cretaceous age. Cristobalite is found sporadically in the Clay Spur bed. In general the presence of cristobalite is not indicated by any visual characteristics.

X-RAY DIFFRACTION DATA

The samples have been centrifuged in order to separate into the size fractions $<1\mu$, $1-5\mu$, and $>5\mu$. X-ray powder diffraction of these fractions on oriented slides and on randomly powdered samples revealed that all the samples have a very similar mineralogical composition. They consist mainly of α-cristobalite and a smectite with small amounts of kaolinite. Semiquantitative X-ray diffraction analyses of the samples indicate that the fine fractions ($<5\mu$) contain about 70% smectite and 20% α-cristobalite, and the coarser fractions ($>5\mu$) consist of about 80% α-cristobalite and 20% smectite. The kaolinite occurs mainly in the $<5\mu$ fractions. Detrital minerals like quartz, feldspars are present in the coarse fractions. Dolomite was identified in the coarse fractions of the Italian and Yugoslavian bentonites.

Because of the very similar mineralogical composition, the samples will not be described separately in the following pages. Instead, the characteristics of the major minerals will be described in details.

α-Cristobalite

X-ray powder diffraction data obtained with a Philips diffractometer, display reflections corresponding to the spacings 4·04 Å (101), 3·14 Å (111), 2·84 Å (102), 2·49 Å (200), 1·61 Å (301) and 1·496 Å (302). These are reflections characteristic for α-cristobalite. The indices of reflections shown in parantheses refer to the primitive tetragonal cell with the space group $P4_12_12$. The most interesting feature of the X-ray diffraction pattern is the profile of the (101) reflection of this mineral. This profile displays a noticeable diffuse scattering towards the lower angle causing broadening of this reflection. This is quite readily seen in Fig. 1 for the samples from Italy and Mozambique, and it indicates the presence of stacking disorder in the α-cristobalite. In Fig. 1 there appears also an additional reflection corresponding to 3·82 Å indicating the presence of another silica phase namely tridymite. This however, does not mean that tridymite exists as a separate mineral in the sample; but it is rather related to the stacking disorder in α-cristobalite. It is known that cristobalite formed at lower temperatures show extensive stacking disorder (Flörke, 1955; Flörke, 1967). Structurally, these two forms of silica are very similar, namely cristobalite displays ABC . . . stacking sequence of $[SiO_4]$ layers, and tridymite an ABAB . . . . stacking sequence. Stacking disorder, if it is present in considerable amount may not only cause broadening and shift of the (101) reflection of α-cristobalite but also may lead to the appearance of the above mentioned tridymite reflections. This is believed to be the case in the above samples. This kind of

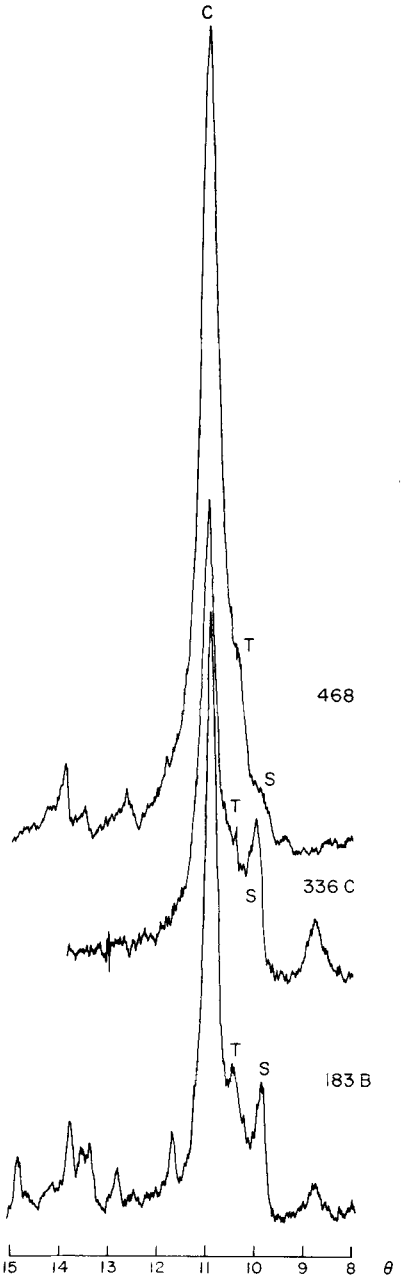


Fig. 1. Profile of the (101) reflection of α-cristobalite showing a pronounced broadening towards the low angle in samples No. 183B, No. 336C and No. 468. C – cristobalite; T – tridymite; S – smectite.

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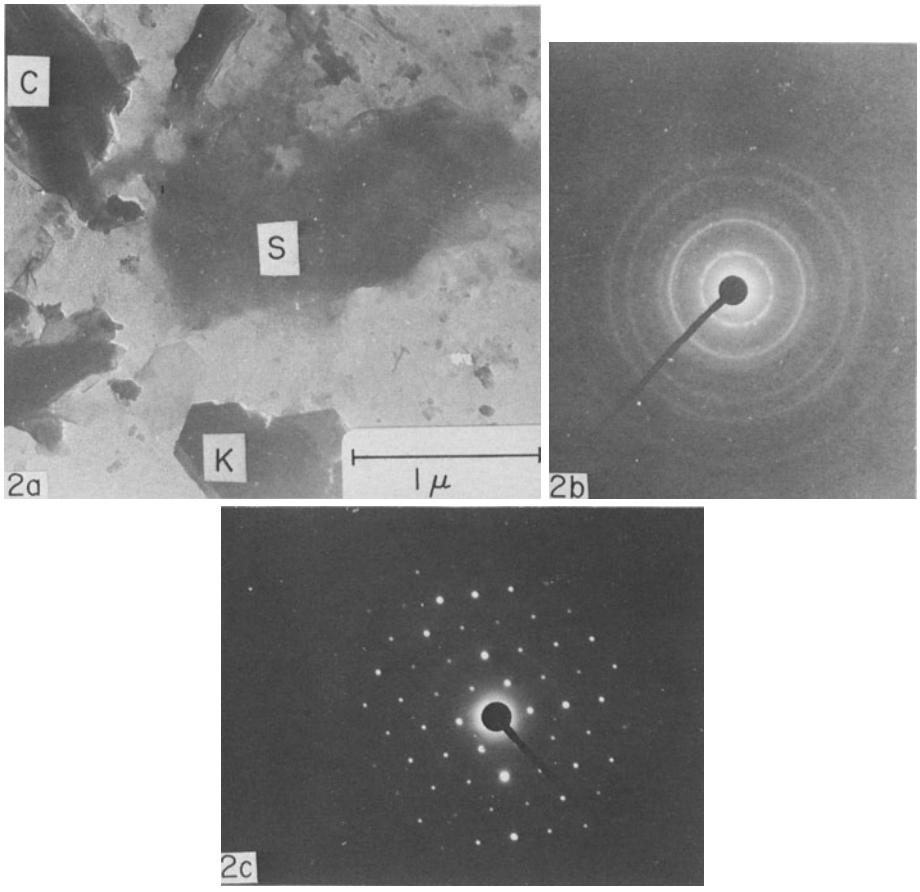


Fig. 2a. Electron micrograph of typical aggregates of smectite (S) and cristobalite (C) in sample No. 336C. Minute and large idiomorph darker grains are kaolinites (K).

Fig. 2b. A SAD pattern obtained from a part of the aggregate (S) shown in the Fig. 2 (Rings of Au-coating are also recorded).

Fig. 2c. The SAD pattern of the large euhedral kaolinite (K) in Fig. 2a (A diffraction ring of Au-coating is also seen).

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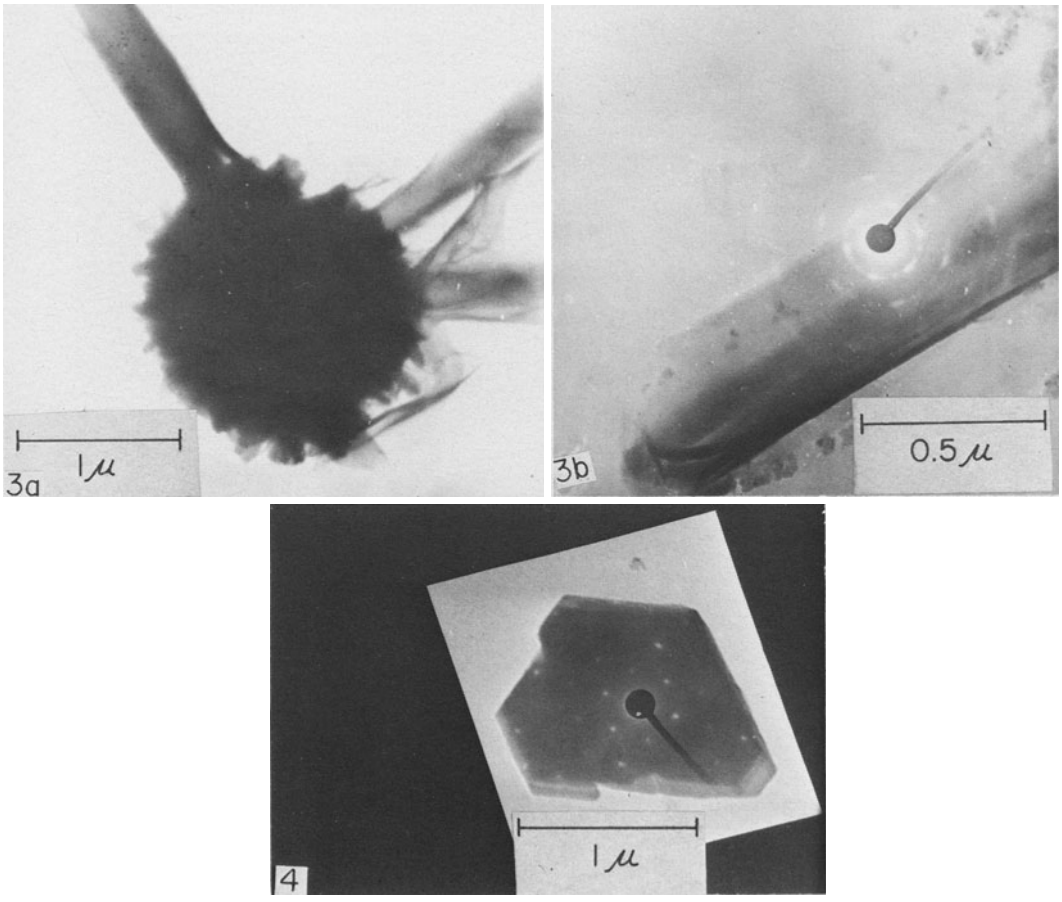


Fig. 3a. Electron micrograph of an intergrown aggregate of tiny crystallites with larger elongated smectite flakes (sample No. 336C).

Fig. 3b. A magnified image of the smectite in Fig. 3a with its superimposed SAD diffraction pattern.

Fig. 4. Electron micrograph of a euhedral kaolinite crystal in the sample No. 468 with its superimposed SAD pattern.

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tridymite reflections do not appear however, on the X-ray diffraction diagrams of the samples from Yugoslavia and Wyoming. In these samples α-cristobalite shows only a small amount of stacking disorder.

An attempt was made to separate α-cristobalite from the rest of the sample in the fractions $>5\mu$ using a liquid of proper density ($\rho = 2{\cdot}40$) which is a mixture of bromoform and carbon tetrachloride. Under the polarizing microscope small aggregates which appeared to be pure α-cristobalite were picked out and they were X-rayed in a Debye–Scherrer camera. The photographs of the samples No. 183B, No. 336C and No. 516 showed clearly the 4·47 and 2·57 Å reflections indicating the presence of smectite in these cristobalite aggregates. Thus cristobalite and smectite form very fine intergrown aggregates in these samples. Cristobalite aggregates in the samples No. 302 and No. 468 do not however show any smectite reflections on the Debye–Scherrer films.

Smectites

This clay mineral forms up to 70% of the fractions $<5\mu$. The X-ray diffraction data collected at room temperature and 50% relative humidity are summarized in the following.

Smectites in Italian bentonites (No. 183B, and No. 336C) have a basal spacing varying between 13·4 and 14·6 Å. Upon ethylene glycol saturation the basal reflection expands to 16·6–17·0 Å, which also shows higher order reflections at 8·5 Å (002) and 5·5 Å (003).

Smectites in Yugoslavian bentonite (No. 302) are characterized by a basal spacing varying between 12·3 and 14·3 Å which expands, upon ethylene glycol saturation, up to 16·6 Å. The second and third order reflections show at 8·4 and 5·5 Å. These are probably more accurate values than the first order reflection, for small angular errors in measurements in the lower angle region result in large errors in the spacing.

Smectites in Mozambique bentonite (No. 468) are present in relatively small amounts which is probably not more than 30%. They have a basal spacing varying between 13·0 and 13·9 Å in the air dried state which expands up to 16·0–17·5 Å upon ethylene glycol saturation.

Smectite in Crook County, Wyoming sample (No. 516) is characterized by a basal spacing of 14·7 Å at room temperature, which then expands up to 17·7 Å upon ethylene glycol saturation.

Kaolinites

In the $<5\,\mu$ fractions of the samples, kaolinites occur as a minor phase. The kaolinite content does not exceed 10% in these fractions. The 7·1 Å and sometimes also 3·58 Å reflections appear in the samples and display rather weak relative intensities. The definite identification of this mineral has been made on the electron micrographs described in the next section.

ELECTRON OPTICAL OBSERVATIONS

A JEM 7 electron microscope, equipped with a field limiting aperture, makes it possible to obtain both transmission micrographs and selected area diffraction (SAD) patterns from areas as small as one micron square. Suspensions of the samples were prepared in a mixture of water and tertiary butylamine in the ratio 700:1. A drop of this suspension was dried on formvar film, and gold and carbon coatings have been used. The most interesting features of the electron optical observations are: (1) Aggregates of cristobalite and smectites. (2) Euhedral kaolinite crystals. These will be now described in detail.

Aggregates of smectite and cristobalite are shown on Fig. 2a from sample No. 336C which represent the most common aggregates in all samples. Thin fluffy aggregates of smectites are shown on the center of Fig. 2a. The selected area diffraction from several parts of this aggregate, Fig. 2b, shows only diffraction rings characteristic of a smectite. These diffraction rings correspond to 4·47, 2·51 and 1·49 Å spacings. The thick platy aggregates with sharp edges are most likely cristobalites. There is however no diffraction ring from cristobalite even from the thinner parts of these aggregates although strong reflections are observed on X-ray diffraction pattern. The fact that the strong (101) reflection from α-cristobalite does not show up might be explained if the orientation of cristobalite atomic planes (101) is perpendicular to the electron beam like the orientation of the (001) plane from the smectites. Then the $[SiO_4]$ layers of cristobalite will be parallel to the (001) plane of smectites on the electron microscope grids.

Figure 3a is an electron micrograph from another aggregate from the Italian bentonite (No. 336C). It shows small cristobalite crystallites of the order of 0·1–0·2 μ intergrown with larger elongated thin flakes. The SAD of these elongated flakes give again diffraction rings typical for smectite (Fig. 3b).

In Fig. 2a, there are also crystals with regular hexagonal habit which are kaolinites. Figure 2c shows the SAD pattern of the kaolinite crystal seen on the lower part of Fig. 2a. Figure 4 shows another euhedral kaolinite found in the Mozambique sample (No. 468) with the SAD pattern superimposed on the same plate. This kind of idiomorph kaolinite crystals is found in all the samples described above. The SAD pattern of these kaolinites indicate an excellent crystallinity

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of these euhedral crystals. This type of kaolinite crystals associated with smectites were observed once before by Altschuler (1963) in natural clay minerals.

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Résumé—Les produits d'altération de matériaux volcaniques provenant de diverses localités du Wyoming (U.S.A.), d'Italie, de Yougoslavie et du Mozambique sont essentiellement des smectites et des cristobalites avec de petites quantités de kaolinite.

La smectite et la cristobalite forment des agrégats séparés et interdéveloppés, de microcristallinité. La diffraction des rayons X montre que la silice est de l'α-cristobalite avec un désordre d'empilement notable. De petits agrégats de α-cristobalite optiquement pure, séparés avec un mélange approprié de bromoforme et de tétrachlorure de carbone, ont révélé contenir, par diagrammes photographiques Debye–Scherrer, une quantité notable de smectite, ceci pour les échantillons provenant d'Italie et du Wyoming (U.S.A.).

Les micrographies électroniques par transmission et les clichés de diffraction électronique de zones sélectionnées montrent, en plus d'agrégats de smectite—α-cristobalite, la présence de cristaux uniques idiomorphes de kaolinite.

Kurzreferat—Veränderungsprodukte aus vulkanischen Materialien von verschiedenen Orten in Wyoming U.S.A., Italien, Jugoslavien und Mozambique sind hauptsächlich Smektite und Cristobalite mit geringen Mengen von Kaolinit.

Smektit und Cristobalit bilden separate und verwachsene Aggregate von Mikrokristallinität. Röntgenbeugungsstudien zeigen, dass die Kieselsäure α-Cristobalit mit merkbarer Schichtungsunordnung ist. Kleine Aggregate von optisch reinem α-Cristobalit, die durch eine geeignete Mischung von Bromoform und Tetrachlorkohlenstoff getrennt wurden, weisen einen beträchtlichen Gehalt an Smektit auf, laut Debye–Scherrer Beugungsphotographien von Proben aus Italien und Wyoming U.S.A.

Transmissions-Elektronen-Mikrophotographien und ausgewählte Flächen-Elektronenbeugungsphotographien zeigen neben Smektit und α-Cristobalit Aggregaten, die Gegenwart idiomorpher Einzelkristalle von Kaolinit.

Резюме — Продукты изменения вулканических пород из различных месторождений Ваиоминга (США), Италии, Югославии и Мозамбика представлены, главным образом, смектитами и кристобалитами с небольшой примесью каолинита.

Смектит и кристобалит образуют обособленные выделения и срастания микрокристаллических агрегатов. Рентгенографическое исследование показало, что кремнезем представлен α–кристобалитом со значительной разупорядоченностью упаковки. Небольшие агрегаты оптически чистого α–кристобалита (образцы из Италии и Вайоминга), выделенные подбором соответствующей смеси бромоформа и четыреххлористого углерода, как показало рентгенографическое исследование методом порошка, содержат заметное количество смектита.

Как следует из электронной микроскопии на просвет и картины микродифракции, помимо агрегатов смектита и α–кристобалита, в изученных образцах присутствуют отдельные кристаллы каолинита.

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