CLAY MINERAL STABILITY AND FORMATION DURING WEATHERING

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ABSTRACT

Clay minerals undergo significant changes when exposed to weathering agents. Some of these changes were revealed by studying a sequence of samples collected from weathering profiles developed on shales. Illite and chlorite are modified by the development of expandable layers within the illite and chlorite structures. The suggested mechanism of alteration of chlorite is the oxidation and removal of octahedral iron. Chemical analyses indicate that interlayer potassium is removed from illites. Removal of potassium may be accomplished by an exchange reaction between potassium ions and hydronium ions in the environment.

The origin of underclays is controversial. In an attempt to shed some light on this subject, three shale-underclay profiles were studied. The changes in elay minerals from shales to underclays are very similar to those in weathered shale profiles. This similarity lends support to the theory that some underclays are products of weathering.

INTRODUCTION

Weathering has been defined in many ways by different people. Jackson and Sherman (1953) defined weathering as the changes in degree of consolidation and in composition which take place in the earth's crust within the sphere of influence of atmospheric and hydrospheric agencies.

A study of the changes undergone by clay minerals of glacial tills under the influence of weathering was carried out by Murray and Leininger (1956), who studied three profiles representing immature, intermediate, and mature stages of weathering in a temperate climate. The results of their study showed that illite and chlorite changed to montmorillonite as the intensity of weathering increased.

Five profiles were chosen for this project. Two of the sections are weathering profiles developed on shales of Mississippian and Pennsylvanian age. The remaining three sections are shale-underclay profiles of Pennsylvanian age.

X-ray diffraction techniques were used for elay-mineral identification. The clay-size fraction of the samples was separated by sedimentation and allowed to settle on glass slides to obtain oriented specimens. Chemical analyses were carried out by x-ray fluorescent spectroscopy and routine wet chemical methods.

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X-ray fluorescent spectroscopy was carried out using powdered whole samples ground to pass a 140 N.B.S. sieve. A lithium fluoride diffracting crystal was used for the elements determined by this method, which were Fe, Mn, Ti, Ca and K. Calibration curves were prepared from samples of known chemical composition, and no internal standard was used.

DESCRIPTION AND MINERALOGY OF PROFILES

Weathering Profiles

Of all common sedimentary rocks, shales contain the largest proportion of clay minerals. For this reason, the weathering profiles developed on shales were selected for study. Profile A is located near Newport in Vermillion County, Indiana. The shale on which the weathering profile was developed is Pennsylvanian in age. A layer of loess overlies the weathered shale, so that weathering of the shale was apparently in progress before the advent of glaciation. The section is 32 ft thick ; samples were collected every foot.

Figure 1 shows selected diffractometer traces of samples from Profile A. The major clay minerals in the shale are illite, kaolinite and chlorite. Significant changes in the clay minerals are evident as the degree of weathering increases. Chlorite and illite break down with concurrent formation of mixed-layer material. This mixed-layer clay contains the parent clays plus an expandable component as shown by the changes which take place on heating and glycolation.

Samples from profile B were collected near Brooklyn in Morgan County, Indiana. The shale is part of the Mississippian Borden Group. The profile is 9 ft thick and was sampled every foot. The dominant clay minerals of profile B are illite, chlorite, kaolinite and mixed-layer clays (Fig. 2). With increase in intensity of weathering, both illite and chlorite are altered by development of interstratified expandable layers forming a mixed-layer structure.

Shale-Underclay Profiles

Many theories have been advanced to explain the origin of underclays, but none of these theories has been universally accepted. On the assumption that underclays are the result of weathering, three shale–underclay profiles were sampled to see if the changes in clay minerals compared in any way to surface weathering profiles.

Samples from Profile C were collected from a pit near Lewisport, Hancock County, Kentucky. The total section is 10.5 ft thick, composed of 6 ft of shale overlain by 4.5 ft of underclay. The most abundant clay minerals are illite, kaolinite, chlorite, and mixed-layer clays (Fig. 3). Some illite and chlorite are altered to expandable layers in the underclay, and the extent of this alteration seems to increase from the bottom to the top of the profile.

Profile D is located near Cannelton in Perry County, Indiana. This shale– underclay section is 8.3 ft thick and was sampled every foot. Figure 4 shows diffractometer traces of the clay minerals in this profile. Kaolinite, illite,



FIGURE 1.—Smoothed x-ray diffractometer traces of selected samples from profile A.



FIGURE 2.—Smoothed x-ray diffractometer traces of selected samples from profile B.





FIGURE 3.—Smoothed x-ray diffractometer traces of selected samples from profile C.

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chlorite and mixed-layer clays are the dominant clay mineral components of this profile. Significant changes in the illite and chlorite are evident in Fig. 4 from the bottom to the top of the profile. The 14Å peak in sample D-9 seems to be from vermiculite, because the reflection is relatively unaffected by treatment with ethylene glycol, but heating at 200° for one hour affects it drastically.

Samples from Profile E were collected near Centerpoint, Clay County, Indiana. The section sampled consists of 1.5 ft of shale overlain by 4.5 ft of underclay. Samples were taken every 0.5 ft Kaolinite, illite, chlorite and mixed-layer clay minerals are the significant components of the profile (Fig. 5). Chlorite seems to be present in minor amounts at the bottom of the profile but is almost completely replaced by mixed-layer material toward the top. Illite is progressively modified toward the top by addition of expandable layers within the structure.

DISCUSSION OF RESULTS

The most significant change observed in the clay minerals from the profiles studied is the alteration of both illite and chlorite by the introduction of expandable layers into the original lattices and the consequent modification of their diffraction peaks. Effects of the alteration of chlorite are seen in the increasing diffuseness of the 14Å reflection and the influence of glycolation and heat treatment on the 001 peak.

Introduction of expandable layers in the illite structure results in asymmetry of the 001 peak toward the low-angle side, broadening of the 002 peak, and asymmetry of the 003 peak toward the high-angle side as described by Bradley (1954). This type of mixed-layer structure has been termed segregated mixed-layer to distinguish it from regular or random mixed-layer structures. Regular mixed-layer structures are composed of a regular alternation of distinct sheets resulting in a superlattice. Random mixed-layer structures are made up of distinct sheets of one clay mineral type randomly disposed in a *c* crystallographic direction. Segregated mixedlayer materials are characterized by variable densities of secondary layers in all crystallographic directions, so that a diffraction band is produced, rather than a peak. The segregated mixed-layer materials are composed of illite and an expandable component and chlorite and an expandable component. It is conceivable, however, that any clay mineral altering to another could form a segregated mixed-layer structure.

A mechanism for the alteration of chlorite and illite, suggested by Murray and Leininger (1956), depends on the oxidation of iron in octahedral positions in the structures. This mechanism is probably operative in chlorite, but some illites may not contain sufficient iron in octahedral positions to cause significant alteration to montmorillonite.

Weathering environments are generally acidic in nature, providing an unlimited supply of hydronium ions. The radii of hydronium $(1.4-1.5\text{\AA})$ and potassium (1.33\AA) ions are similar, so that an exchange may be set up





⁷IGURE 5.—Smoothed x-ray diffractometer traces of selected samples from profile E.

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between hydronium ions in the environment and the potassium in interlayer positions in illite. This exchange apparently would proceed by mass action, owing to the abundance of hydronium ions in the environment as compared to potassium present in illite. If hydronium ions have replaced potassium in interlayer positions, the layers would probably not be bound as tightly because of the slightly greater size and the somewhat polar nature of the hydronium ion. This may allow water to enter between the layers, expanding the lattice and producing layers similar to hydrogen montmorillonite which are present as "islands" in the illite structure. The chemical analyses (Table 1) show that potassium percentage decreases with increase of weathering, thus tending to substantiate this interpretation.

Sample Number	${ m SiO}_2$	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO_{2}	CaO	MgO	K ₂ O	Na ₂ O
A3	54.1	21.0	7.95	0.10	0.79	0.073	1.98	3.35	0.93
A-7	51.4	21.7	8.40	0.13	0.86	0.073	2.20	3.50	0.87
A-9	53.7	20.9	8.40	0.13	1.00	0.058	1.83	3.25	0.87
A-11	52.9	22.9	9.15	0.16	0.92	0.055	1.83	3.40	0.74
A-13	64.2	17.4	6.70	0.051	0.94	0.031	1.10	2.55	1.11
B-2	56.4	20.2	7.00	0.068	0.78	0.25	3.17	3.95	0.93
B-4	53.4	19.6	7.40	0.085	0.75	0.39	3.72	4.30	0.78
B-6	55.1	19.6	7.15	0.063	0.79	0.35	3.42	4.20	0.82
B-8	57.1	19.7	8.40	0.080	0.96	0.090	2.14	4.17	0.82
C-2	55.8	22.2	5.65	0.042	0.92	0.058	2.07	3.77	0.27
C-5	49.7	21.2	10.25	0.094	0.87	0.050	2.19	3.60	0.23
C-8	60.0	21.2	3.30	0.030	1.05	0.042	0.85	2.76	0.20
C-11	60.7	22.5	1.95	0.012	1.10	0.017	0.43	2.30	0.20
D-2	51.0	28.0	4.50	0.061	0.93	0.053	1.19	2.98	0.27
D-5	65.6	20.2	3.20	0.020	1.06	0.042	0.70	2.80	0.17
D-7	71.6	16.6	1.60	0.010	0.98	0.017	0.70	0.38	0.17
D-9	65.0	20.8	1.75	0.010	1.20	0.030	0.27	1.15	0.20
E-3	66.5	15.4	7.60	0.059	0.98	0.047	0.70	2.60	0.13
E-5	58.7	16.8	10.75	0.082	0.86	0.069	0.79	2.72	0.15
E-8	62.3	23.1	1.80	0.010	1.12	0.028	1.10	2.70	0.24
E-10	60.7	23.9	1.80	0.016	1.16	0.030	0.92	1.93	0.19
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TABLE 1,-PARTIAL CHEMICAL ANALYSIS OF SELECTED SAMPLES

Results from the analysis of the shale–underclay profiles are inconclusive in respect to origin, but seem to indicate that the underclays studied are weathered material, either transported to a basin of deposition or developed by subaerial weathering of the underlying shale before formation of the coal swamp.

SUMMARY

1. Illite and chlorite in the shales studied are progressively altered under the influence of weathering by formation of expandable layers within the crystallites, resulting in a mixed-layer structure.

2. Analyses of shale-underclay profiles show that mixed-layer clays are present in the underclays and are more prevalent near the top of the underclay. This would seem to substantiate the theory that underclays are formed as a result of weathering.

3. The mechanism by which illite and chlorite are changed to mixed-layer clay containing expandable layers is either oxidation of iron in the octahedral layers or the replacement of potassium in illite by the hydronium ion.

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