SAPONITE FROM THE DALRADIAN META-LIMESTONES OF NORTH-EAST SCOTLAND

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ABSTRACT: The Dalradian meta-limestones of the Banffshire coast have been investigated as part of a study of the mineralogy of Scottish sedimentary and metamorphic rocks, the main purpose of which is to assess the extent to which soil minerals are inherited from such parent rocks. Saponite was found to be a common constituent of the non-carbonate fraction. Thin sections of the limestones were examined microscopically and the textural relationships between the saponite and the other minerals, particularly those of undoubted metamorphic origin, suggest that the saponite was formed during the metamorphism. Recent reports of the hydrothermal synthesis of saponite at elevated temperatures and pressures support this hypothesis.

INTRODUCTION

The Dalradian rocks of Scotland are generally considered to range from the late Pre-Cambrian to Cambrian in age. In the Banffshire region they consist of an extremely thick succession of a wide variety of rock types, the stratigraphy of which has been described by Read (1936). The Lower and Middle Dalradian rocks have been strongly metamorphosed and comprise great thicknesses of quartzites, flags, schists, gneisses and limestones. The Upper Dalradian, however, is markedly less affected by metamorphism and consists of some 14,000 ft of greywackes, shales, andalusite-schists, grits, calcareous flags and limestones. The structure of the area is extremely complex and possibly involves nappe formation, recumbent folding and sliding on a gigantic scale (Read, 1955). The clay fractions of the calcareous rocks of the mildly metamorphosed Upper Dalradian division were found to be rich in smectites. Subsequently, the study was extended to cover the calcareous rocks of the Lower and Middle Dalradian which had hitherto been regarded as extremely unpromising material for clay minerals. The object of this paper is to describe the nature of the clay minerals within these rocks and to discuss the conditions of their formation.
The location of the area and of the limestone outcrops sampled are shown in Fig. 1. The group names and approximate stratigraphic positions of the limestones are listed below.

- Whitehills Group: Upper Dalradian (lower part)
- Boyne Limestone: Upper Dalradian (lower part)
- Portsoy Group: Middle Dalradian (middle part)
- Sandend Group: Lower Dalradian (upper part)

Studies of the non-carbonate rocks in the Dalradian sequence of the Banffshire coast show that they have been subjected to metamorphism of variable intensity (Read, 1923). Thus, immediately above the Whitehills Group there occur extensive developments of andalusite-mica-schist. However, both the Sandend and Portsoy Groups are associated with kyanite- and staurolite-schists; furthermore the Portsoy Group is directly overlain by a biotite-gneiss occasionally containing sillimanite and cordierite. The metamorphism therefore ranges widely and Read (1952) believes that it was characterized by conditions of high temperature and low directed pressure, possibly related to the height of a migmatite front.

METHODS OF INVESTIGATION

The rock samples were crushed to <150 μ and 25 g amounts digested in 400 ml of 1:3 acetic acid after the method of Gault & Weiler (1955). Usually, two such treatments were required to digest the carbonates; the presence of dolomite increased the time of extraction considerably. In order to establish that acetic acid treatment did not affect the clay minerals two limestone samples were also extracted using the di-sodium salt of EDTA and by ion exchange resins. X-ray photographs of the clay fractions acquired by these two methods showed no appreciable difference from the acetic acid-extracted clays and it was therefore concluded that
the latter treatment had no effect upon the clay minerals. After carbonate removal
the insoluble residues were centrifuged and washed several times and the $<1.4 \mu$
fraction separated using the standard sedimentation procedures of Mackenzie (1956)
with a few drops of ammonia as a dispersant. Sufficient washing of the insoluble
residue is extremely important as acetates may persist in the clay fraction in the
forms of calcium acetate hemi-hydrate, magnesium acetate ($\beta$ form) and ammonium
acetate. The strongest X-ray lines of the first two acetates are at 16.7 and 10.2 Å,
respectively, with the result that they may be mistakenly identified as glycerol-
expanded montmorillonite and mica. Complete acetate removal was confirmed in
several samples by the lanthanum nitrate test described by Vogel (1941, p. 307).

X-ray powder photographs of pressure-oriented aggregates of the $<1.4 \mu$ fraction
were taken in 9 cm precision cameras using a Raymax diffraction unit and Co $K\alpha$
radiation. The differential thermal curves were obtained using the apparatus des-
cribed by Mitchell & Mackenzie (1959) in a nitrogen atmosphere with a heating
rate of 10° C/min and the electron microscopy of the clay fraction was studied
with an A.E.I. EM 6 instrument. The 50–150 $\mu$ fraction was separated into light
and heavy fractions using tetrabromoethane (specific gravity 2.95) and examined
optically. Carbonate minerals were identified by the staining technique of Warne
(1962).

RESULTS

General petrography and mineralogy

In the Whitehills Group the limestone is medium grained, crystalline and
arenaceous with many large corroded quartz crystals showing undulose extinction.
Calcite is the predominant carbonate although there is a small amount of dolomite.
Occasional black carbonaceous matter is scattered throughout the rock along with
iron oxide minerals, tremolite laths and a little biotite. The Boyne Limestone is
medium grained, crystalline and strongly banded, and foliated. It consists of a
mosaic of calcite and phlogopite, with many oriented prisms of tremolite and diopside
and is traversed by narrow bands of small interlocking quartz crystals. Other
minerals present in small amounts are epidote, clinozoisite, chlorite, muscovite,
titanite and albite. In the Portsoy Group two limestones were sampled near an
exposure of anorthosite. Both are coarsely crystalline with roughly equal amounts
of calcite and dolomite, and scattered grains of talc and tremolite. However, the
more westerly sample contains felted masses of chlorite with quartz, iron oxides,
titanite, apatite and zircon in minor amounts; further to the east the limestone
contains abundant oriented laths of phlogopite with small amounts of sphalerite,
pyrite, biotite and anthophyllite. In the Sandend Group the limestones are medium
to coarse grained, and contain calcite as the sole carbonate. They are foliated
and display oriented laths of phlogopite and muscovite. Other minerals present
are quartz, iron oxides and sometimes tremolite, talc and chlorite. Tourmaline,
apatite, plagioclase feldspar and anthophyllite occur in minor amounts.
X-ray results

The diagnostic basal reflections of the <1·4 \( \mu \) fractions before and after glycerol treatment may be seen in Table 1. These results are broadly representative of the clay minerals in several other limestones investigated within each particular group although not all the limestones examined contained smectite. It may be seen that glycerol brings about an expansion of the basal spacing from 14 to 18 \( \AA \) approximately. Heating to 300\( ^\circ \) C in a capillary tube, followed by immediate sealing to prevent rehydration, caused a contraction of the basal spacing to about 10 \( \AA \) and a similar contraction was induced by saturation with K\( ^+ \) ions. These features are all characteristic of the smectite group of clay minerals. Furthermore, a consistently strong (060) line at 1·53–1·54 \( \AA \) indicates a trioctahedral variety. Spectrochemical analysis of a clay from the Portsoy Group limestones showed it to be magnesium rich indicating either saponite or hectorite. However, the latter contains structural lithium and since the analysis showed only trace amounts of this element it was concluded that the smectite mineral was saponite.

Table 1 also shows the presence of other lines at approximately 14, 9·4 and 8·5 \( \AA \) indicating chlorite, talc and tremolite, respectively. These minerals also occur, sometimes in abundance in the 50–150 \( \mu \) fraction and may also be seen in thin section.

Finally, it may be noted that the Sandend sample shows a broad line at 12·03 \( \AA \) which is replaced by a more sharply defined line at 12·4 \( \AA \) on glycerol treatment and by one 10·7 \( \AA \) on heating to 500\( ^\circ \) C for 2 hr. This may be interpreted in
terms of a three-component random interstratification apparently consisting of smectite, because of the effect of glycerol, and chlorite, since heat treatment does not cause a complete collapse to 10 Å or below. The third component is either mica or talc, probably the latter in view of its presence as a separate mineral in the clay fraction.

**Differential thermal analysis**

Differential thermal curves for the clay minerals from the Boyne Limestone, largely smectite, and for saponite from Staffin, Skye are shown in Fig. 2. Ignoring the endothermic reaction at 268°C in the latter sample, due to a small amount of gibbsite, it will be seen that the two curves are generally similar although peak temperatures are rather different. The appreciable difference in the high temperature endothermic reactions may possibly be due to the presence of chlorite in the Boyne Limestone sample.

![Differential thermal curves](image)

**Fig. 2.** Differential thermal curves. (a) <1-4 μ fraction of Boyne Limestone; (b) saponite from Staffin, Skye (small amount of gibbsite present).

**Electron microscopy**

Electron micrographs showing the characteristic morphology of the clays are seen in Plate 1 (a and b). Thin flakes are predominant with ill-defined and fluffy appearance; they often have curled edges and are occasionally aggregated. This appearance is typical of montmorillonite minerals although saponite studied by Mackenzie (1957) was elongated along the a axis. Occasional well-defined flakes are also seen, probably representing the minor amount of talc detected by the X-ray powder method. The needle or fibre-like crystals are almost certainly tremolite.

**Optical microscopy**

Thin sections of the limestones were made so that the optical and textural characteristics of the minerals could be studied. The saponite occurs as dark fine-grained aggregates, sometimes with a pale pink or greenish tinge and occasionally deep brownish red. Its refractive index is lower than that of Canada balsam (<1.53), and its mode of occurrence varies considerably. In the Whitehills Group
Limestone it is present as sparsely scattered discontinuous aggregates within the calcite matrix, sometimes sharply abutting against the larger quartz particles (Plate 2 a and b). The clay patches are more densely distributed and of a more uniform size in the Sandend Limestone, imparting a definite clotted texture (Plate 2 c). Where the rock is strongly foliated as at Fordyce these aggregates tend to be elongated with stretched calcite grains (Plate 2 d). This is even more distinct in a tremolite-schist west of Sandend where streaked-out saponite aggregates are folded in unison with oriented mica laths (Plate 2 e). In the Portsoy Limestone the smectite also occurs in aggregates, but occasionally it is interleaved with phlogopite (Plate 2 f) and sometimes with chlorite.

**DISCUSSION**

The results have established that a trioctahedral smectite, probably saponite, commonly occurs in the clay fractions of the unweathered meta-limestones of the Banffshire coast. In general, smectites are considered to originate in environments of low temperature and pressure. Thus Ross & Hendricks (1945, p. 71) state that ‘montmorillonite . . . is predominantly a product of weathering formed in the presence of liquid water’ and that ‘where there is evidence that minerals of the montmorillonite group were formed by thermal processes there is every reason to believe that they were deposited late in the paragenetic sequence when the temperature was low, that is as much as 200° C but in general below that temperature’. On the other hand, however, hydrothermal syntheses have been achieved by a number of workers at more elevated temperatures and pressures. In the system MgO–Al₂O₃–SiO₂–H₂O, Roy & Roy (1955) found that montmorillonite of variable composition may be stable at about 350° C and that substitution of magnesium in the structure extended the stability range to 480° C. Ames & Sand (1958) investigated the factors governing the maximum hydrothermal stability of smectite and showed that the presence of alkali cations in saponites increased the decomposition temperature from 300° to 750° C. Koizumi & Roy (1959) formed a montmorillonite mineral above 550° which persisted to 850° C at 1000 atm and Iyama & Roy (1963a) synthesized a trioctahedral sodium smectite in the system Na₂O–MgO–Al₂O₃–SiO₂ which was stable up to 850° C. All the above syntheses were accomplished using mixtures of gels, oxides and glasses, but recently Levinson & Vian (1966) have shown that smectites, probably trioctahedral, may be easily synthesized at 300° C using various carbonates, quartz and kaolinite and reactants. These studies all indicate the possibility that, provided compositional requirements are fulfilled, smectites may form as primary minerals in medium or high grade metamorphic rocks (Iyama & Roy, 1963a, p. 170).

A metamorphic origin for the saponite of the Banff meta-limestones is indicated by its association with talc, phlogopite and chlorite, minerals of the same structural type, related chemical composition and of undoubted metamorphic formation. A more intimate structural relationship is exhibited in the Sandend Limestone where smectite is found in random interstratification with chlorite and probably
Electron micrographs. < 1.4 μ fraction of Portsoy Limestone. (a) general field; (b) flakes showing ill-defined form and curled edges.

(Facing p. 348)
Photomicrographs. (a) Whitehills limestone; irregular patches of saponite. × 21. (b) Whitehills limestone; saponite patches abutting against quartz crystal. × 63. (c) Sandend limestone; saponite aggregates giving a definite 'clotted' texture. × 21. (d) Sandend limestone — Fordyce; saponite aggregates streaked out in a foliated limestone. × 63. (e) Tremolite-schist — Oran Quarry; saponite aggregates streaked out and folded. × 63. (f) Portsoy limestone; saponite occurring as aggregates and also intercalated in a phlogopite flake. × 63.
talc, clear evidence of a concomitant origin. Furthermore, it must be emphasized that talc, chlorite and phlogopite are all found in equilibrium with smectites in the various phase assemblages worked out from hydrothermal synthesis (Roy & Roy, 1955; Iiyama & Roy, 1963a). Even the interstratified clay minerals may be regarded as stable phases (Iiyama & Roy, 1963b). A metamorphic origin is also more consistent with textural relationships revealed in thin section (Plate 2). Indeed, the occurrence of the saponite in the form of dense randomly distributed aggregates is strongly reminiscent of similar textures which are a familiar feature of early thermal metamorphism.

The possibility must be considered that the saponite may have been present in the rocks before metamorphism either as a result of inheritance, i.e. as a detrital mineral, or by diagenesis. However, the first theory demands the persistence of a saponite-rich source area throughout many millions of years of geological time; the second argues continued existence of unusual diagenetic conditions throughout a similarly long period. On the other hand the process of metamorphism has affected the whole sequence of Dalradian rocks and all that is required for the formation of saponite is the existence of limestones of appropriate chemical composition. Following Levinson and Vian (1966) it may be postulated that the smectite was formed by some such reaction as:

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\text{Dolomite} + \text{Kaolinite} + \text{Quartz} + H_2O \rightarrow \text{Calcite} + \text{Smectite} + CO_2.
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REFERENCES