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**MICROSTRUCTURE OF BILLINGS SHALE AND BIOCHEMICAL
ALTERATION PRODUCTS, OTTAWA, CANADA**

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Microstructure of Billings Shale and Biochemical Alteration Products, Ottawa, Canada

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A microstructural analysis has been made of altered and unaltered black shale from a site where foundation heave has occurred. Jarosite framboids composed of very small interlocking crystals, much larger crystals of gypsum and microorganisms are described in the altered shale. The relative roles of jarosite, gypsum, and other hydrated sulphates in the generation of heave forces is not fully understood. If jarosite is responsible, most black shales have a heave potential; if gypsum is responsible only black shales which contain carbonate need be of concern. Recognition of fungi and other microbes suggests a more complex biogeochemical cycle than previously supposed; the use of microorganisms as a method of controlling heave warrants more investigation.

On a fait une analyse microstructurale d'un schiste noir altéré et non altéré provenant d'un site où un soulèvement de fondation s'était produit. Des framboïdes de jarosite composés très petits cristaux enchevêtrés, des cristaux beaucoup plus gros de gypse et des microorganismes sont identifiés dans le schiste altéré. Les rôles respectifs de la jarosite, du gypse et d'autres sulfates hydratés dans la génération des forces de soulèvement ne sont pas clairement définis. Si la jarosite est responsable, la plupart des schistes noirs sont susceptibles de gonfler; si le gypse est responsable, seuls les schistes noirs contenant des carbonates doivent être considérés. L'identification de champignons et d'autres microbes suggère un cycle biogéochimique plus complexe que ce qu'on supposait; l'utilisation de micro-organismes comme méthode de contrôle des soulèvements nécessite des études supplémentaires.

[Traduit par la Revue]

A black shale of Ordovician age known as the Billings Formation has been associated with heave of lightly loaded structures in Ottawa, Ontario (Penner *et al.* 1970, 1973; Quigley and Vogan 1970; Quigley *et al.* 1973). Similar problems with black shales and other materials such as fly ash backfill have been described from other localities in this country and abroad (Moum and Rosenquist 1959; Fairbridge 1968¹; Spanovich and Fewell 1969; Jangdal 1971; Fasiska *et al.* 1974). Black shales are known from many geographic localities and formed at geological ages ranging upwards from the Precambrian (Pettijohn 1957).

Reaction products and the acid conditions at the site in Ottawa together with past and present experience indicate that autotrophic

bacteria are probably in part responsible for the degradation of the shale (Ivarson 1973) and accompanying volume increase which leads to the generation of heaving forces. Despite detailed investigations in a number of laboratories the mechanism of the biogeochemical reactions is not fully understood (Penner *et al.* 1970, 1973; Quigley and Vogan 1970; Quigley *et al.* 1973; Napier and Wakerley 1969; Pochon and Jatton 1967). The purpose of this paper is to describe the microstructure of the shale and alteration products at the site of the Bell Canada building in Ottawa and to discuss the mechanism of heave of black shales.

Composition of Unaltered and Altered Shale

A range of samples was examined from relatively fresh to severely rotted specimens which were coated with secondary alteration prod-

¹Fairbridge, R. W., Columbia University, New York, N.Y., personal communication.

ucts. Hand specimens were studied on a stereopolarizing microscope, standard thin sections were examined on a Leitz Orthoplan petrographic microscope, and fracture surfaces were observed on a scanning electron microscope (Cambridge Stereoscan Mk II). Samples for examination on the scanning electron microscope were coated with a conductive layer of gold/palladium to minimize charging.

The mineralogy and chemistry of similar samples had been previously established by powder X-ray diffraction analysis using camera and diffractometer methods of recording and by standard chemical techniques. The principal minerals in the unaltered shale are illite, chlorite, quartz, calcite, and pyrite. In the altered shale gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, are the most abundant new minerals though there is also evidence on X-ray diffractograms for some development of a mixed-layer swelling clay mineral; the content of calcite is markedly decreased. The main conclusions from the chemical analyses are that pyritic sulphur is present in both altered and unaltered shale; that sulphate sulphur is present in the altered but not in the unaltered shale and that there is a marked decrease in carbonate content (estimated as inorganic CO_2) between the unaltered and altered shale. The content of organic carbon is high relative to that of nonblack shales.

Optical microscopic examination of relatively unaltered Billings shale shows it to be a dark fine-grained rock. In thin section the well-developed preferred orientation of the phyllosilicates is clearly apparent. Pyrite sometimes showing cubic morphology is present locally in large amounts. The altered rock is softer and displays many white crystals of gypsum and accumulations of yellow jarosite. The jarosite appears to be cryptocrystalline and sometimes in thin section single or multiple rounded aggregations can be seen. Elsewhere it is intimately associated with the much larger gypsum laths surrounding them and occasionally coating cleavage planes. In places it appears as if secondary replacement of gypsum by jarosite had occurred along the cleavages. Alteration products frequently are located near pyrite indicating precipitation after only a short diffusion path through solution of reacting ionic species.

Scanning electron micrographs of unaltered Billings shale are shown in Fig. 1A–D. Edges of oriented, sometimes bent phyllosilicates which are in places partly obscured by debris can be seen in Fig. 1A on the rock surface fractured approximately normal to the bedding. Figure 1B illustrates the appearance of the rock when viewed from a direction at right angles to the orientation of Fig. 1A; preferred orientation of the phyllosilicates though not estimated quantitatively is quite apparent. Small cubes of unaltered pyrite are shown in Fig. 1C, D.

The modes of occurrence of the principal alteration products are illustrated in Fig. 1E, F and Fig. 2A–F. In Fig. 1E, F, gypsum forms lath-like crystals which are sometimes coated with small tabular interlocking crystals of jarosite which in morphology almost exactly reproduce textbook illustrations (Palache *et al.* 1957, p. 560). At low magnification fibroidal texture can be seen in places on surfaces of the altered rock and an individual spheroid composed of very small pseudooctahedral and pseudotetrahedral crystals, probably of jarosite, is shown in Fig. 2A, B. A distribution of secondary minerals is shown in Fig. 2C and enlargements in Fig. 2D–F. The 'flower-like' morphology appears to be produced by a regular intergrowth of tabular crystals. Other minerals such as gypsum have been described with a similar morphology on the macroscale. An elemental analysis with a Kevex electron microprobe indicated that the 'flowers' contain both iron and potassium reinforcing the suggestion that they are probably jarosite.

In Fig. 3A–F microstructures are illustrated which appear to be biological in nature. The organism attached to the jarosite spheroid is probably a fungus but of uncertain nature (Fig. 3A–C). The object in Fig. 3D is possibly a bacterium. It differs from those previously observed by the authors, however, in that it is about four times as long and does not appear to have collapsed in the high vacuum; it may also have a protuberance and seems to be attached to the rock. It seems more probable that it is a fungal spore. The nature of the objects in Fig. 3E and F is uncertain but most probably they are biological.

Discussion

Black shales are relatively rich in organic

(a) MICA-TYPE MINERALS (Perp. to Bedding)

(b) MICA-TYPE MINERALS (Parallel to Bedding)

(c) PYRITE CUBES

(d) PYRITE CUBE

(e) GYPSUM

(f) GYPSUM AND JAROSITE

FIG. 1. Scanning electron micrographs of minerals in Billings Shale, Bell Canada Building, Ottawa, Canada.

(a) SPHEROIDAL STRUCTURE

(b) EUHEDRAL CRYSTALS COMPOSING SPHEROID

(c) GYPSUM AND JAROSITE IN SHALE

(d) JAROSITE AND MICA-TYPE MINERALS

(e) JAROSITE

(f) JAROSITE

FIG. 2. Scanning electron micrographs of microstructure of rotted Billings Shale, Bell Canada Building, Ottawa, Canada.

(a) SPHEROID WITH ATTACHED FUNGUS OR ACTINOMYCES

(b) FUNGUS OR ACTINOMYCES

(c) MYCELIUM ON MICROCRYSTALS OF SPHEROID

(d) (?) FUNGAL SPORE

(e) STRUCTURES OF UNKNOWN NATURE

(f) DETAIL IN STRUCTURES OF UNKNOWN NATURE

FIG. 3. Scanning electron micrographs of microbiological objects in Billings Shale, Bell Canada Building, Ottawa, Canada.

matter and have a carbon content of 3% or more. They also contain a considerable amount of iron sulphide which is usually present as pyrite. Typically there is not much carbonate but in some layers or lenses the quantity becomes significant sometimes in association with concretions, nodules, and cone-in-cone structure (Pettijohn 1957). It is generally agreed that rocks of this sort formed in an anaerobic environment but numerous explanations have been advanced to account for the way in which conditions were established which led to the very low oxidation-reduction potential implied by the mineral assemblage. Availability of organic matter to sulphate reducing bacteria, diffusion regime, and reactivity of iron minerals are probably significant in favoring formation of sedimentary pyrite in these rocks (Berner 1970). In the altered shale the two minerals which form in conspicuous amounts are gypsum and jarosite. The swelling clay mineral detected in altered shale by X-ray methods seems to be present in too small an amount to be responsible for heave though such products should not be ignored when heave mechanism is considered.

The heave which accompanies weathering of black shale has been attributed by some authors to the oxidation of pyrite because calculations indicate a large increase in volume when the sulphide is converted to hydrated sulphates such as jarosite or other minerals containing different cations which have been shown to be precipitated (Fasiska *et al.* 1974). In this interpretation some authors assign only a passive void-filling role to the gypsum (Pettijohn 1957, p. 363; Spanovich and Fewell 1969, p. 15). Spanovich and Fewell worked on black shales in Pennsylvania, West Virginia, and eastern Ohio and recognized a series of five chemical reactions with formation of melanterite, rozenite, coquimbite, jarosite, and limonite as oxidation products of pyrite. They also identified gypsum and kaolinite as secondary products. They stated that "the reaction produces gypsum that generally forms bluish white rosettes. The expansion of pyritic shales is sometimes erroneously attributed to the formation of these gypsum crystals which only inhabit voids vacated by earlier dissolved minerals." The opposite viewpoint has also recently been advanced, (Quigley *et al.* 1973,

p. 1014). These authors working on black shales at Ottawa concluded that "... it appears clear that growth of gypsum crystals within the shale is the primary cause of heave.

The abundant, rather spectacular yellow and orange jarosite and natrojarosite deposits do not themselves appear to have caused any heave as they coat voids within the shale and between the gypsum crystals."

Resolution of this issue is of practical as well as theoretical importance. If heave is caused by formation of gypsum black shales which are free of calcite can be considered 'safe' from the engineering point of view since the supply of Ca^{++} ions will be limited to those available on exchange sites and the amount of gypsum formed should be rather small. If this is the correct mechanism this type of heave phenomenon should be relatively uncommon since most black shales contain little carbonate. Furthermore a potentially expansive black shale may be recognized simply by analyzing the rock for carbonate and precautions taken when required. Conversely pyrite is very common in this sort of rock and if pyrite oxidation is the principal cause of heave most black shales are capable of swelling if conditions exist or are created during construction which are favorable to growth of oxidizing bacteria.

Gypsum is most commonly formed in nature by precipitation from concentrated seawater together with other salts. It is still uncertain whether anhydrite rocks originate by dehydration of primary gypsum or whether they form directly from anhydrite precipitated at somewhat higher temperatures than gypsum from saturated brine solutions. It is, however, established that secondary gypsum rocks form by rehydration of anhydrite deposits by ground waters percolating to depths of a few hundred feet. The volume relations between anhydrite and gypsum deposits have recently been reviewed by Holliday (1970). While the unit cell of gypsum is considerably larger than that of anhydrite he concludes that in general the hydration reaction proceeds by a volume for volume process the excess sulphate being removed in solution.

The chemistry of formation of gypsum in black shale appears to be rather straightforward involving attack on calcite by sulphuric

acid formed by the oxidation of pyrite. Hence if gypsum crystallization causes the volume increase of black shale which contains carbonate there are only a few possible ways of avoiding heave. One is to prevent acid formation by guarding against the establishment of oxidizing conditions; another is to neutralize acid should it form by some alternative chemical reaction which is not accompanied by crystallization of solid products of increased volume under the conditions at the construction site. Alkali has been used in this way by the present authors (Penner *et al.* 1973). It is also evident that either of these procedures should effectively prevent jarosite formation.

Jarosite belongs to the alunite group of minerals which have a considerable range of composition. The structure can tolerate substitution of ions of a variety of sizes providing suitable adjustments to charge balance are made to preserve electrical neutrality. The minerals are commonly secondary and form as alteration products which result from weathering or hydrothermal action. Jarosite is insoluble in water. A summary of some of the modes of occurrence of jarosite has been given by Hutton and Bowen (1950).

Jarosite has been synthesized at temperatures as low as 110 °C from an acid solution of ferric sulphate and potassium sulphate (Fairchild 1933) and basic ferric sulphates occupy the central portion of the $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ phase diagram (Posnjak and Merwin 1922).

The potassium is generally considered to be derived from micas or mica-type clay minerals and recent work with the electron microprobe confirms that potassium may be released by biotite during the formation of jarosite (Rimsaite 1973). The precipitation of basic sulphates also implies dilution and local increase of pH.

Sulphate ions for jarosite formation may be supplied from any source such as seawater (Fleming and Alexander 1961). When the mineral has a paragenesis in black shale it is thought that the sulphate is derived by oxidation of iron and other metal sulphides.

Iron in the ferric state is also necessary and the oxidation of ferrous sulphate (formed from FeS_2) to ferric sulphate proceeds only very slowly or not at all at normal temperatures in

the absence of a catalyst or iron oxidizing bacteria (Silverman and Ehrlich 1964). Sulphuric acid is formed in the oxidation reactions and produces an environment favorable to the growth of this type of bacteria. It has been suggested that the oxidation of pyrite may follow a different course in a calcareous and in a noncalcareous environment. When lime is present gypsum forms together with iron hydroxides whereas jarosite and iron hydroxides are believed to be the main reaction products when lime is absent (Miedema *et al.* 1973).

Jarosite evidently forms in black shale only if a rather special set of conditions is established. The initial production of sulphuric acid and ferrous sulphate results from oxidation of the pyrite and this reaction may proceed chemically. It is probable, however, that thio-bacilli are also involved. These bacteria are probably most active in the early phases of the reaction and ferrobacilli only play a dominant role later when fall in pH due to production of sulphuric acid has created conditions which favor their growth. The recognition of fungi on the scanning electron microscope suggests that these organisms also have a function but its nature is not yet clear.

If, however, it is correct to attribute heave to jarosite formation the more complex chemical and biochemical sequence of reactions invite consideration of more ways of breaking the chain which leads to expansion than is the case if gypsum is the causative agent. Since microorganisms may be in part responsible for the mineralogical changes their use in heave prevention might be explored. For example, fungi have been shown to take up K^+ ions from phyllosilicates (Weed *et al.* 1969). Likewise they have been held responsible for a fall in Eh in leaching of alum shales. Marked Eh gradients over distances of a few inches were detected and were accompanied by conversion of ferric iron to ferrous iron even though low pH conditions which favored continued growth of ferrobacilli were maintained (Napier and Wakerley 1969). If fungi could either take up sufficient K^+ ions preferentially or induce low Eh conditions jarosite formation should be hampered or stopped. In one case there would cease to be a supply of K^+ ions and in the other the availability of ferric ions would terminate. The nature of the fungi in these rocks is not known

but if they are of this variety it may be possible to alter conditions so as to further stimulate their growth. Alternatively inoculation of the rock with a favorable strain may be feasible. In any event if crystallization of jarosite does indeed generate the expansive forces successful growth of a favorable strain of fungi in the shale either by stimulation of those already existing or by addition of a suitable variety should prevent or curtail heave of the shale.

Conclusions

1. Heave of black shales results from the formation of secondary minerals of increased volume formed in association with the bacterial oxidation of pyrite and production of sulphuric acid.

2. The main reaction products are gypsum and jarosite.

3. It is not certain which of these minerals generates heave pressure.

4. If jarosite is responsible most black shales are potentially capable of heave; if gypsum is responsible only those black shales which contain significant quantities of carbonates need be considered.

5. Resolution of point 4 is of practical importance to the building industry since carbonates may be easily detected and potentially expansive rocks readily identified.

6. Recognition of fungi on the scanning electron microscope suggests a complex biogeochemical cycle in the rock.

1. Biochemical means should be explored as a possible method to control heave.

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