The Rapid Weathering of a Siltstone

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ABSTRACT. The rapid weathering of an excavated siltstone at Liddell, New South Wales, was investigated. Framboidal pyrite in the siltstone was intimately associated with carbonate minerals, mainly dolomite. It seems that the pyrite was oxidised by air, water and probably iron-oxidising bacteria to form sulfuric acid which reacted with the carbonate minerals to form gypsum and epsomite. These chemical changes together with some expansion effects caused the breakdown of the siltstone.

INTRODUCTION

The rapid breakdown of some excavated rock at Liddell has been investigated. Liddell is about 90 km northwest from Newcastle, which is about 130 km northeast from Sydney, New South Wales. The Permian sedimentary rocks are in an area near the base of the Mulbring Subgroup and are mainly sandstones overlain by siltstones.

SAMPLING

The samples of siltstone were taken near the site for the Liddell Power Station, prior to its erection. Brief details of the samples include the initial description at the time of sampling and the designation, based on a mineralogical examination, in terms of the classification given by Williams, Turner and Gilbert (1955).

Sample A is siltstone (subfeldspathic lithic wacke) which was freshly removed by jackhammer from a slope.

Sample B is a siltstone (subfeldspathic lithic arenite) which was collected similarly to Sample A, at the same level but 15 m away from it.

Sample C is a siltstone (subfeldspathic lithic wacke) which was sampled 2 m below the weathered material (Sample D).

Sample D is weathered material from a level 12 m above Sample A.

Sample E comprises several pieces of weathered material which were collected from the slope near the area where samples A to D were taken.

Sample F is a piece of core which was regarded as representative of the basement sandstone (lithic arenite).

METHODS OF ANALYSIS

The mineralogical composition was studied by microscopy using polished section-and thin section-techniques, and by X-ray diffraction. Major elements were determined by X-ray fluorescence spectroscopy, trace elements by atomic emission spectroscopy and carbon and sulfur by chemical methods. The nature of the organic matter was ascertained by a differential thermal analysis-technique (Swaine, 1969) using samples of powdered rock which had been demineralised by treatment with hydrochloric and hydrofluoric acids. An estimate of pyrite (FeS₂) was obtained by determining pyritic iron.

RESULTS AND DISCUSSION

The results of the chemical analyses are given in Table 1. The compositions of the three siltstone samples (A, B, C) are remarkably similar. The highest silicon and the lowest aluminium and iron values are in the sandstone (Sample F), as expected. There is more organic carbon, total sulfur, sulfate sulfur and pyrite in the siltstone samples than in the sandstone sample. The most important differences are the lower values for calcium, carbonate (given as CO₂), organic carbon, total sulfur, sulfate sulfur and pyrite in the weathered siltstone (Samples D and E), compared with the siltstone.

The trace-element contents (Table 2) are not unusual and are mostly between those for an 'average' sandstone and an 'average' shale. These results would seem to indicate that trace elements are not a relevant factor in the weathering of the siltstone. The values for boron in the siltstone, namely, 70-80 ppm, are in the range that has been suggested for coals and associated sediments that have been exposed to brackish water, probably during their early history (Swaine, 1962, 1967, 1971).

Microscopical examinations gave detailed information on the mineralogy of the samples. Sample A is a subfeldspathic lithic wacke. The detritus is composed of quartz (80%) of plu-tonic and volcanic origin, plus volcanic (acid-intermediate) and metamorphic (metaquartzites, schists, gneisses), rock fragments (15%), with feldspars (mainly plagioclase) and micas forming a minor component (2-3%). Detrital calcitic oolites, minor opaques (ilmenite, pyrite and organic matter) also form a minor component (2-3%). Material of argillaceous composition totals 10% of the rock, and cement material, chiefly siderite, weathered to limonite, plus a small fraction of framboi dal pyrite totals 5-10% of the rock. The average grain...
The rapid weathering size of detritus is ~0.1 mm. Some detrital pyrite occurs, but framboidal pyrite is minor. Pyrite is usually intimately associated with the detritus along fractures in quartz grains. It is postulated that siderite and some pyrite were originally de-bilised by recrystallisation of glassy phases. Evidence in other samples.

A carbonate phase has formed by replacement of plagioclase feldspars, and the carbonate plays an important role in cementing the other rocks, siderite forms the main cementing component. A carbonate phase has been associated with pyrite, but the relation is by no means conclusive as to the formation of the pyrite in the detritus, which is certainly of later, diagenetic origin. It would seem that a continuous process is in operation.

Clusters of framboids range up to 100 - 150 μm. Framboidal pyrite occurs ubiquitously in the rock. The chief habit of the pyrite - occurring in the matrix material and in fractures. It is postulated that siderite and some pyrite were originally de-bilised by recrystallisation of glassy phases. Evidence in other samples.

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Organic matter is common in this rock and may reach 10%. The average grain size is 0.03 - 0.05 mm. Larger quartz grains (up to 0.5 mm) are occasionally present. Limonitic spherules, presumably oxidised pyrite, about 10 μm in size, are dispersed in the rock, where its occurrence is controlled by bedding planes, indicating a syngenetic genetic processes in the rock. They both occur from the origin of pyrite within detritus, which is certainly of later, diagenetic origin. It would seem that a continuous process is in operation.

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size of detritus is 0.1 mm.

Some detrital pyrite occurs, but frambooidal pyrite is the dominant habit. The latter is found chiefly in the matrix, but often within volcanic rock fragments and in clusters between detritus. Distribution of frambooids is to a large extent controlled by bedding planes, indicating a syngenetic origin. However, this cannot be clearly separated from the origin of pyrite within detritus, which is certainly of later, diagenetic origin. It would seem that a continuous process is in operation. Pyrite and siderite share an important role in diagenetic processes in the rock. They both occur intimately associated with the detritus along fractures and grain boundaries of rock fragments, and in fractures in quartz grains. It is postulated that siderite and some pyrite were originally deposited in the fracture and have since been remobilised by recrystallisation of glassy phases. This means that the siderite-pyrite phase was deposited pre-devitrification in the diagenetic history. The sample chronology is supported by evidence in other samples.

Particle size of pyrite as frambooidal aggregates varies between 15 μm and 1 μm, with a mode of 5 μm. Clusters of 5 μm frambooids reach 80 μm across. Individual 'crystallites' making up the frambooids have a relatively constant size of 1-2 μm. Organic material is relatively common and fragmentary. Pyrite is sometimes associated with organic matter, but no strict association of either with the other can be discerned. The organic material has a size range 30 - 200 μm with a mode around 50 μm.

Sample B is a subfeldspathic lithic arenite. The detritus is composed of quartz (80%), volcanic and metamorphic origin, volcanic (andesine, anorthoclase) and metamorphic (microcline)feldspars (5%), and volcanic and metamorphic rock fragments (15%). Organic material, oolites, and shell fragments together form a minor component. Oolites show a concentric growth structure, nucleated on fine quartz grains. Argillaceous material totals 5 - 10% of the rock and cement material (mainly siderite) ~5% of the rock. The average grain size of the rock is 0.2 - 0.3 mm.

The chief habit of the pyrite - occurring mainly in the matrix - is frambooidal. Detrital pyrite is minor. Pyrite is usually intimately associated with the siderite cement. Frambooid size varies between 5 and 35 μm. It was noted in this sample that the 'crystallites' making up the frambooids had, probably, an octahedral habit and were relatively constant in size (1 - 3 μm). Clusters of frambooids range up to 100 - 150 μm. Siderite occurs ubiquitously, intimately associated with the matrix material and in fractures. Plagioclase grains are frequently replaced by a carbonate, probably calcitic. Organic matter is often associated with pyrite, but the relationship is by no means conclusive as to the formation of individual frambooids. Only the smaller frambooids are associated with organic material.

Sample C is a fine grained subfeldspathic lithic wacke. The detritus is composed mainly of quartz (80%), volcanic and metamorphic rock fragments (15%), and minor feldspars and micas (5%). Argillaceous matrix material totals 15% of the rock, and cement material, mainly siderite, totals 10%. The average grain size is 0.05 - 0.05 mm.

Frambooidal pyrite occurs ubiquitously in the matrix, though its concentration is highly variable. Limited areas show large (0.5 mm) clusters of minute frambooids. One such cluster has a semi-ordered array of 2 μm frambooids interspersed with octahedral crystals of comparable size. Individual crystals making up the frambooids are sub-micron size (~0.03 μm) and difficult to resolve, but the octahedral crystals occurring with them are uniformly of 2 - 3 μm size and comparable to crystallites in the larger frambooids in this and other rocks, implying that they have a similar origin. Organic matter is common in this rock and may reach 2 - 3%. Some structure is present, and is not associated to any great degree with pyrite. As in the other rocks, siderite forms the main cementing agent and is intimately associated with all the components of the rock. A carbonate phase has formed by replacement of plagioclase feldspars, probably a calcite carbonate, as no limonite alteration is seen.

Sample D contains fine grained quartz, muscovite and feldspars in a matrix of limonite and clay. Larger quartz grains (up to 0.5 mm) are occasionally present. Limonitic spherules, presumably oxidised frambooids, are dispersed in the matrix.

Sample E contains quartz, muscovite, feldspars and rock fragments in a limonitic clay matrix. Translucent brown limonite spherules, presumably oxidised pyrite, about 10 μm in size, are common.

Sample F is compositionally classified as a lithic arenite. A grain size classification would place it in a fine grained conglomerate class, with average grain size 2.5 mm. The detritus is composed of volcanic and metamorphic (gneissic) rock fragments (40-50%), quartz (plutonic and metamorphic 40%) and minor feldspars, micas and opaques (10%). Matrix material of argillaceous composition is minor, and cementation is effected by a siderite-limonite mixture, supplemented by welding of the detritus. Calcite replaces nearly all of the feldspars (including microcline in gneissic rock fragments) to some extent.

Some detrital pyrite occurs, but frambooidal pyrite is conspicuous by its absence, especially in the matrix of the rock, where its occurrence is rare. The only significant occurrence of pyrite is in volcanic rock fragments, where it exhibits similar features to that in other rocks. Pyrite, where present varies from 2 - 15 μm (mode 3 μm). Siderite and limonite replace iron in the matrix of the rock, and as cementers, constituting ~15% of the rock. They occur as limonite-stained siderite nodules generally 10 μm in diameter, with limonite as an alteration product of siderite giving it a deep red colour. Their origin would appear to be diagenetic, possibly
replacing pyrite but more likely formed by nucleated growth. Common occurrence is a small volcanic rock fragment between two large quartz grains, cemented by these nodules, and a surrounding siderite mass which is not as limonitised. The replacement is virtually complete, illustrating the high degree with which this rock has been filled with siderite. The critical point in this rock is that virtually no pyrite is present, siderite and limonite being the cement. Organic matter is very low in abundance and rarely has pyrite associated with it.

Mineralogical information obtained by X-ray diffraction is given in Table 3. It should be

| Table 3: Mineral Composition Determined by X-Ray Diffraction |

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**NOTES**
- G means a major constituent of sample
- L means a lesser constituent of sample
- T means a trace constituent of sample
- ? means possibly present
- * means that a trace of pyrite is possible, but all diagnostic peaks are masked by muscovite or other major constituents.

noted that low concentrations of pyrite, say of the order of 1%, are not easily detected by X-ray diffraction in samples of siltstone and sandstone, whereas pyrite is readily detected by the polished- and thin section-techniques as used in microscopy. It is not always easy to identify particular carbonate minerals by microscopy, but X-ray diffraction is usually specific, provided that the mineral is present at a concentration of at least about 1%. Hence, it is considered that dolomite (Ca, Mg (CO₃)₂) is the main carbonate mineral in the siltstone samples (A, B, C), although siderite (FeCO₃) was reported using microscopy. There may be traces (less than about 1%) of calcite (CaCO₃) and siderite in the siltstone samples. Calcite was detected in two other samples of siltstone not considered above. Pyrite in the siltstone samples is largely framboidal, that is, it is made up of discrete, spheroidal aggregates of microcrystallites of FeS₂. Framboidal pyrite from a Liddell siltstone is shown in the two scanning electron micrographs, (Figs. 1a and 1b). Fig. 1a shows a cluster of framboids, each one being about 15 μm in diameter. The raspberry-like texture is shown well in Fig. 1b of a single framboid, the microcrystallites being about 2 μm in diameter. Some of the microcrystallites are angular, rather than rounded; such variations in shape and in size have been reported for framboids in shales (Love and Amstutz, 1966).

At the level of a few per cent of carbon in rocks it is difficult to ascertain the form of carbon by X-ray diffraction. However, this may be done by a differential thermal analysis-technique (Swaine, 1969). The carbon in the siltstone samples was shown to be in the form of bituminous coal. This is not surprising since the sediments are near bituminous coal seams.

X-ray diffraction was carried out on some handpicked material. A white layer removed from some rock fragments contained dolomite and a trace of pyrite. Vein material and crystals from the weathered zone were mainly gypsum (CaSO₄.2H₂O). This explains the low calcium and sulfate in the weathered samples (D, E). Evidently the gypsum was precipitated from solution in discrete areas rather than evenly disseminated. Thin white crust on pieces of siltstone that were weathering contained epsomite (MgSO₄.7H₂O).
THE RAPID WEATHERING

The results given above may be summarised concisely. The weathered siltstone contains less calcium, carbonate, carbon and sulfur than the siltstone. The pyrite and carbonate minerals (mainly dolomite) in the siltstone are not in the weathered material, which contains gypsum and epsomite. These observations suggest that the pyrite has been oxidised to produce some sulfuric acid which has reacted with the dolomite to form gypsum and epsomite. The oxidation of pyrite is complicated and incompletely understood (Lowson, 1982), but the following reactions, although simplified, cover the main points (Swaine, 1979):

(a) \[ 2\text{FeS}_2 \cdot 7\text{O} \cdot 2\text{H}_2\text{O} = 2\text{FeSO}_4 \cdot 2\text{H}_2\text{SO}_4 \]

(b) \[ 4\text{FeSO}_4 \cdot 0\text{H}_2\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \]

(c) \[ 14\text{Fe}^3+ + \text{Fe}_2\text{S}_3\text{H}_2\text{O} = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16 \text{H}^+ \]

(d) \[ \text{Fe}_2(\text{SO}_4)_3 + (3+x)\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + x \text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 \]

Reaction (b) is slow unless there is a catalyst present. It has been proposed by Singer and Stumm (1970) that iron-oxidising bacteria, for example, *Thiobacillus ferrooxidans*, can catalyse the oxidation of ferrous to ferric iron. Details of this process are given by Lundgren and Dean (1979). The ferric iron oxidises pyrite (reaction c) and is also hydrolysed to give hydrated iron oxide (reaction d). These two reactions yield sulfuric acid which keeps the pH down to below about 3 which favours the optimum growth of the bacteria. The *Thiobacillus ferrooxidans* bacteria seem to be attached selectively to pyrite surfaces (Gormely and Duncan, 1974) thereby being readily available to catalyse the oxidation of ferrous iron, as soon as the pH is lowered by the formation of sulfuric acid (reaction a).

In the presence of oxygenated water, where the redox potential (Em) is about 0.4v, pyrite is relatively unstable (Hem, 1960). The large surface area of frambooidal pyrite (Fig. 1b) allows ready access of water and air (oxygen) which would promote oxidation of the pyrite. The rate of oxidation of pyrite (dG/dt) depends on several factors (Swaine, 1980) and can be expressed as

\[ \frac{dG}{dt} = (\text{FeS}_2)_n \times [O_2], \text{SS}_3 \text{H}_2 \text{O} \times \text{pH}, \text{T}, \text{MB}, \text{SA}, \text{OM} \]

where \([O_2]\) = concentration of oxygen, \(\text{SS}_3 \text{H}_2 \text{O}\) = surface saturation with water, \(\text{pH}\) = acidity, \(\text{T}\) = temperature, \(\text{MB}\) = microbiological factors, \(\text{SA}\) = surface area and \(\text{OM}\) = other minerals present. The important factors in the weathering of the siltstone are the availability of air, water and probably iron-oxidising bacteria. The close association of the frambooidal pyrite with carbonate minerals, mainly dolomite, has enhanced the neutralisation of sulfuric acid to form gypsum and epsomite. The coaly matter in the siltstone has also been oxidised (Table 1), but it has not been possible to ascertain if this reaction has enhanced or retarded the oxidation of pyrite. The role of water may be that of a reaction medium or its main function may be 'to provide a means by which the oxidation products are desorbed (dissolved) from the pyrite surface' (Nordt and Smith, 1966).

However, water takes part in reactions (a), (c) and (d), so it should be seen as essential for the complete oxidation to proceed.

CONCLUDING REMARKS

The Liddell siltstone seems to be unusual in having frambooidal pyrite intimately associated with carbonate minerals, mainly dolomite. Exposure to air, water and, probably, suitable iron-oxidising bacteria caused rapid deterioration of the siltstone. The oxidation of the pyrite released sulfuric acid which reacted with the dolomite to form gypsum and epsomite. Since the oxidation products occupied a greater volume than the pyrite, some expansion must have taken place. The resultant weathered material should be reasonably stable. The siltstone in situ should not oxidise if air and water are excluded and seepage water would be very low in oxygen, because of bacterial breakdown of organic matter at the sediment-water interface. There could also be bacterial reduction of sulfate ions when conditions are anaerobic. It is salutary to recall the statement by Krauskopf (1967) that 'we can decipher what happens chemically in the decay of a rock, but we have no means of predicting accurately what the state of the rock will be at a particular time in the future'. However, at Liddell there is no further evidence of weathering of the siltstone since excavation ceased, which would seem to endorse the above suggestions for keeping oxidation at a minimum.

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INTRODUCTION


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