WEATHERING OF CHLORITE TO CHLORITE/SMECTITE MIXED-LAYERS IN PROTEROZOIC METAPELITES - A LINK BETWEEN ACID DEPOSITION AND ROCK DETERIORATION?

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SUMMARY
Clay minerals occurring in proterozoic metapelites at outcrops near Enköping, ~70 km NW of Stockholm, Sweden, were studied by XRD. Horizontal to subhorizontal surfaces on outcrops in the area were decorated with rock-carvings (e.g. ships, human and animal figures) during the Bronze Age (1500-500 B.C.). According to archaeologists, deterioration of Bronze Age artifacts has been accelerating during this century. Mica-rich rock surfaces belong to the most affected. As a consequence of acidified deposition, chemical weathering and mineral transformations may have a prominent role in the deterioration of the rocks. Surface samples from exposed rocks and short drill-cores were studied for possible mineralogical changes, for instance, the occurrence of expansible layers in phyllosilicates, which can be assumed to result from alteration of biotite or chlorite under acidic weathering conditions.

The rocks in the study area are composed of decimeter to meter thick alternating beds of metapelites and metaarenites, which during Proterozoic have undergone medium-grade regional metamorphism, ~600°C, 3.5-4 kbar. In terms of abundance the following minerals are about equally represented: extensively chloritized biotite, sodic plagioclase, muscovite and quartz.

Separation of the <2mm, and occasionally the <0.2mm fraction, was achieved after coarse crushing and partial ultrasonic disintegration of specimens. Clays were Mg²⁺ saturated and diffractograms of oriented samples were recorded after ethylene glycol solvation and (hydrazine) treatment. Identification of clays was based on matching with calculated patterns from NEWMOD.

Muscovite, chlorite, chlorite/smectite mixed-layers, plagioclase, quartz and jarosite were identified in the suite of samples. However not all phases were simultaneously present in all samples. The suite of samples is assumed to represent different stages in the alteration of an initially Fe-rich chlorite via Fe-loss to a random chlorite/smectite interstratification, with a successively growing fraction of smectite component in the mixed-layer. Reduction of the fraction of hydroxide-layer present in the chlorite gives the interlayer space between two 2:1 layers a smectite-like character. Depth distribution of the ethylene glycol-swelling 2:1 layers in two 30 cm drill-cores shows, that the smectite-like material coincides with open fissures. An increase in the amount of swelling clays may contribute to the accelerated deterioration of the rocks.

1. INTRODUCTION

During an ongoing survey on the condition and deterioration phenomena of rock-carvings in Uppland, Sweden, special attention has been given to objects on outcrops in the Rickeby area, since these have been well documented by photography from the 1920:s and onwards. Different deterioration phenomena such as scaling, rounding of contours and deepening of carved figures are repeatedly observed. Mica or phyllosilicate rich outcrops appear to be the most damaged which stresses the importance of the structure and mineralogy of the rock. The causes for the deterioration of the hitherto preserved objects are unclear and may be found in several changes of their near environment. These changes include occasional removal of the soil or vegetational cover which may have protected against freezing and gives access to mechanical damage caused for instance by visitors or grazing cattle or to changes in the chemistry of weathering by increased atmospheric pollution.

Loosening of the grain structure is often the underlying cause for rock deterioration and therefore mineral alteration by chemical weathering was considered of interest since these processes may lead to changes in volume and thereby lead to movements between grains. The local rock is rich in chlorite and mica and pedogenic weathering of chlorite into vermiculite and smectite is well known (e.g. Herbillon and
These hydrated clays may change in volume depending on wetting and drying and their formation by alteration of the primary minerals is often accompanied by the formation of Fe-oxides or hydroxides in the rock (Proust et al., 1987). The objective of this study was to identify possible weathering effects on the mineralogical composition of the rocks, such as the transformation of the primary mica and chlorite into hydrated clay minerals.

2. STUDY AREA

The studied sites with bronze-age rock-carvings with their age estimated between 1500 and 500 BC are situated in an area of several square kilometers at Rickeby in the vicinity of the church of Boglösa southeast of the town of Enköping and about 70 km north-west of Stockholm, Sweden. Flat bedrock-outcrops of roughly 5 to 50 m² in size occur in grass-land and are surrounded by clayey soils. The dominating rock is the area consists of alternating decimeter to meter thick bands of metaarenites (oligoclase-rich quartzite) and metapelites (mica-schists). Due the banded character of the rock the mineralogical composition varies within short distance. The amounts of the major minerals are in the following ranges: 15-30% quartz, 10-40% oligoclase, 15-30% biotite and chlorite, 10-40% muscovite (Stålhös, 1974). The mineralogical compositions reflects medium-grade regional metamorphism caused by the intrusion of granitic plutons and the age of the rock is roughly 1.8 Ga.

3. SAMPLES

It was difficult to obtain rock-specimens with a hammer from the smooth and rounded surfaces of the outcrops. Therefore three types of samples were collected. Solid, apparently unweathered rock fragments obtained with a hammer. Loose fragments of hand-specimen size that had become detached by scaling, and diamond-drill cores of about 30 cm length on a selected outcrop. The rocks were crushed into sub-cm pieces with hammer, no grinding was employed. These pieces were further fragmented with an ultra-sonic probe so that individual grains were loosened to a great extent. From suspensions of this material clay fractions separated by centrifugation. From selected sections of the drill-cores polished thin sections were cut for microscopy.

4. METHODS

The clay fractions were prepared for x-ray diffraction by saturation with Mg²⁺. These were also analyzed after treatment with ethylene-glycol for identification of expandable clays. Selected sample were treated with hydrazinehydrate to check for presence of kaolinite. The preparation of oriented samples was according to the membrane-filter transfer method (Drever, 1973). In the interpretation of the diffraction patterns from the oriented samples the program NEWMOD 2 (Reynolds, 1985), which simulates one-dimensional diffraction patterns of interstratified clay minerals, was used.

The silt/sand fraction was used to produce diffractograms of random powder mounts for identification of primary minerals in the samples. Data were collected with a diffractometer generating Cu K-radiation and equipped with a diffracted beam LiF monochromator using the Philips APD software.

5. RESULTS

Examination of thin-sections from the drill-cores shows a thin coating of Fe-minerals on the rock surface. Parallel to and about 1 to 1.5 mm below the surface thin cracks are cutting through the rock except through blades of muscovite. The muscovite thus seems to reinforce the structure of the rock. These cracks are partly filled with opaque material which presumably are Fe-(hydr)oxides. Orientation of the
mica layers perpendicular to the rock surface is common for the outcrops. Muscovite is the more weathering resistant mica and the grains that lie open to the surface have frayed or kinked edges, whereas the biotite grains have a low relief on the surface and smoothly abraded edges. Throughout the rock the biotite is extensively chloritized. The chlorite is commonly filled with opaque spots that again are presumed to be Fe-(hydr)oxides.

The diffraction trace of an oriented sample of the clay fraction from site 138 is shown in Fig. 1. This sample appeared to be representative of unweathered rock and the clays did not respond to EG-solvation. Also shown in the figure are the simulated patterns for a tri-tri-chlorite with peaks at 14Å, 7Å and 4.7Å, and a diocathedral mica (muscovite). The proportions between minerals in the simulation are 79% mica and 21% chlorite, which is a rough approximation because the proportions would change if biotite would be included in the simulation. There is however no way to quantify the amount of biotite in the mixture from the raw data. More interesting is the simulation of the chlorite, since matching of the patterns depends heavily on estimation of the chlorite composition in the simulation. A good fit was obtained with 2.3 Fe (per half unit cell) in the 2:1 layer (Sil Fe= 2.3), 2.5 Fe in the hydroxide sheet (Hyd Fe=2.5) and a complete hydroxide sheet (Hyd=1.0). Chlorite of this composition was assumed to be representative for unweathered chlorite in the study area, but this assumption can not be substantiated due to the small number of samples taken. Minor peaks not matched by the simulation are from quartz and feldspar.

A clay mineral with interlayers that respond to EG-solvation with a peak at 16.2 Å was found for instance in a fragment detached from the surface of site 180. The diffraction trace for this sample is shown in Fig. 2 where a chlorite with a higher ratio between 14Å and 7Å peaks, probably reflecting loss of Fe, is found. A large amount of an expandable clay together with Fe-depleted chlorite from site 176 is shown in Fig. 3 together with a simulation of the composition of the expandable phase. A reasonable match is obtained with a random interstratified chlorite/smectite composed of 60% tri-smectite (1 Fe per half cell and two EG layers) and a highly Fe-depleted tri-chlorite with 1 Fe in the 2:1 layer, 0.2 Fe in the hydroxide sheet and 95% of the hydroxide sheet remaining intact. This chlorite composition is derived from a simulation of a sample dominated by highly weathered chlorite.

A complete simulation of all layer silicates in the sample from site 176 is presented in Fig. 4 and it suggests 45% of muscovite, 30% of the interstratified chlorite/smectite, 15% of the Fe-depleted chlorite and 10% of "unweathered" chlorite. No evidence for kaolinite was found in the hydrazine treated samples.

Two diamond drill-cores, 19 and 30 cm deep, were taken from site 111 to investigate how smectite (or vermiculite) was distributed below the rock surface. In the first core smectite was present in small amounts throughout its 19 cm length. The second core cut two open fractures and ended at a third fracture at 30 cm depth. The highest amounts of the expandable material were found at the surface and in the section between 20 and 30 cm depth which was cut by open fractures. Between 8 and 16 cm no response to EG-solvation was found.

6. DISCUSSION

It is difficult to find direct evidence in the data for a relationship between the weathering of chlorite to smectite or vermiculite and the deterioration of the rock. It is uncertain if the occurrence of the expandable clay is due to weathering, since it may also have formed during late-stage metamorphic reactions. Loose or friable rock evidently contains expandable clay, but its formation does not have to be a recent phenomenon. In the determination of the distribution of clay minerals in the rock the present method has a poor spatial resolution. Several cm² of rock have to be fragmented to obtain sufficient amounts of clay for the XRD analysis. Thus material is bulked over distances that may be much larger than the probably sub-millimeter scale on which mineral alteration may be critical to rock deterioration. Due to this bulking, very high concentrations of vermiculite or smectite in, for instance, fine fractures may be mixed with unweathered chlorite from a larger volume of intact rock.

The types of minerals found are roughly in accord with previous observations of chlorite weathering. The alteration sequence of chlorite to regular interstratified chlorite/vermiculite, later to random interstratified
chlorite/vermiculite and finally to vermiculite was reported by Herbillon and Makumbi (1975). Argast (1991) found high-Fe chlorite to weather directly to vermiculite or hydroxy-Al vermiculite, without interstratified intermediates. Alteration to Fe-oxides and smectite are reported by Proust et al. (1987) and Buurman et al. (1988). The diffraction patterns indicate that Fe-loss has occurred from chlorite in samples were the expandable material is present. In this case the chlorite composition in site 138 is assumed to be representative for the unweathered chlorite in the whole area, which however is uncertain. Loss of Fe, often in conjunction to Fe-oxidation, has been described in association to vermiculitization of chlorite in several studies (Gilkes and Little, 1972; Ross, 1975; Ross and Kodama, 1976; Proust et al., 1986). However, Murakami et al. (1996) found no difference in weathering resistance between Fe and Mg chlorite. Vermiculitization of the biotite may also contribute to the formation of the expandable material (Kalinowski and Schweda, 1996). Rust coatings and other Fe-precipitates show that Fe is continuously released by chlorite or biotite weathering. Occurrence of hydroxy-Al interlayered smectite or vermiculite could neither be confirmed nor ruled out. Once hydroxy-Al interlayers are formed at a certain depth in soils, no coexisting EG-swelling material is usually found. It is intriguing that no such formation of hydroxy-Al takes place in the rock-hosted swelling material. Formation of hydroxy interlayers tends to be inhibited by low pH (<3) and by complex forming ligands (e.g. Barnhisel and Bertsch, 1989). These conditions are probably not represented at the rock surface and at interior surfaces. Since hydroxy-Al interlayers block the expansion of vermiculite and smectite, artificial formation of these interlayers (Barnhisel and Bertsch, 1989) should be considered as a possible treatment to reduce volume changes in smectite or vermiculite rich rocks.

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Figure 1. The diffraction trace of the oriented clay fraction from an unweathered rock from site 138. No response to EG-solvation was shown. The pattern is matched by simulations (dotted lines) of a high-Fe chlorite and dioctahedral mica.

Figure 2. EG-solvation produced a peak with d=16.2Å in material from a detached surface fragment from site 180. A higher 14Å relative to 7Å peak compared to the sample shown in Fig. 1 may reflect a loss of Fe from the chlorite.
simulation:
R0 interstratified
60% tri-smectite, 1 Fe, 2 EG /

tri-tri-chlorite;
2:1 layer: 1Fe
0.2 hyd Fe
95% hydroxide sheet

Figure 3. In several samples the expandable material produced a peak at 16.2Å after EG-solvation. The diffraction pattern for the clay form site 176 is shown with a pattern calculated for a random interstratified chlorite smectite (dotted line). The composition of the components is given in the figure.

Figure 4. The same sample as in Fig. 3 is shown with the combined calculated patterns for the different phyllosilicate components.