



Weathering of glauconite in an alkaline environment — A case study from Krakow area, Poland

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ABSTRACT

The purpose of the study was to investigate glauconite weathering in regolith profile developed on Santonian marls in Zabierzów (South Poland) most likely during Paleogene. Because of the high carbonates content the studied regolith appears to constitute a unique case where glauconite underwent weathering under alkaline conditions.

Unweathered glauconite-bearing marls and regolith profile were sampled. Samples pH was determined for 1:1 rock–water solution. Mineral composition of bulk rock, clay fraction (< 2 and < 0.2 μm) and green pellets separated from bulk rock was determined with X-ray powder diffraction (XRD). Thin sections prepared from the undisturbed bulk rock were examined using optical microscopy. Separated clay fraction and green pellets were analyzed using Fourier transform infrared spectroscopy (FTIR). Mössbauer spectroscopy was used to determine Fe²⁺/Fe³⁺ in unweathered glauconite. Scanning electron microscope with energy dispersive X-ray spectroscopy was used for observation of morphology and chemical analysis of the separated pellets.

Samples were characterized by alkaline reaction (pH between 7.66 and 7.98). XRD analysis of unweathered marls showed presence of calcite, glauconite, quartz, smectite and traces of kaolinite, apatite and pyrite. The weathered material was depleted in glauconite and pyrite while enriched in goethite. Mössbauer spectroscopy showed that oxidation of part of octahedral Fe²⁺ located within the glauconite took place. FTIR spectroscopy showed that in regolith profile intensities of OH-stretching band assigned to glauconite decreased upward while goethite bands intensities increased, relatively to unweathered marls.

In the studied profile glauconite underwent dissolution. Si and Mg were leached out with weathering solution while due to alkaline pH Fe³⁺ crystallized in situ in form of goethite having likely substitutions of Al. Neoformation of smectite-rich mixed layered mica-smectite minerals from the solution was also likely to take place.

1. Introduction

Glauconite is a marine clay mineral which commonly occurs in sediments and sedimentary rocks. Glauconite term is used twofold: as green aggregates (hereafter pellets) or as an end member of a sequence of mixed-layered minerals similar to mica-smectite with minor amount of expandable layers (Burst, 1958; Thompson and Hower, 1975). Glauconite belongs to interlayer deficient mica group i.e. non-swelling, 2:1 layer type having the layer charge between ~0.6–0.85 per formula unit and the interlayer space occupied by non-hydrate monovalent cations (most commonly K⁺ or NH₄⁺). In the structure of glauconite each layer consists of one octahedral sheet sandwiched between two tetrahedral sheets (Guggenheim et al., 2006). The layer charge originates from Al³⁺ for Si⁴⁺ substitutions within the tetrahedral sheet or

Mg²⁺ and/or Fe²⁺ for Fe³⁺ and/or Al³⁺ in octahedral sheet.

Glauconite forms in marine environment of low-latitude shelves and also in deeper parts of the basins (e.g. Burst, 1958; Hower, 1961; McRae, 1972; Odin and Matter, 1981; Odom, 1984; Odin and Fullagar, 1988; Baldermann et al., 2013). Sufficient amounts of K and Fe, small supply of land-driven sediments and redox potential (Eh) near ~0 are required for glauconite formation. Under those conditions Fe-rich smectite (nontronite) is believed to transform into glauconite, by fixation of the K⁺ within the interlayer space. The fixation is considered to be driven by the decrease in the amount of expandable layers in the mineral structure due to an increase of the mineral layer charge caused by reduction of a part of the octahedral Fe³⁺ and incorporation of Mg²⁺ into the structure (Burst, 1958; Thompson and Hower, 1975; Baldermann et al., 2013). Glauconite is unstable in surface and

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subsurface environments and because of that glauconite is believed to be easily weathered in those environments (Komadel et al., 1995; Skiba et al., 2014). Though glauconite rarely constitutes the main soil mineral, it commonly occurs in soils developed from sediment and sedimentary rocks.

In general the mechanism of glauconite weathering is not well understood. Weathering of glauconite has been studied since the very first work performed for the Eocene sands of Virginia, USA, by Gildersleeve (1932) who, using optical microscopy techniques, observed replacement of glauconite grains with iron oxy/hydroxides. Further research were focused also on clay mineralogy of the weathering due to the fact that clay minerals constituted important products of glauconite weathering (Wurman, 1960; Cloos et al., 1961; Hutcheson and Haney, 1963; Loveland, 1981; Courbe et al., 1981; El-Amamy et al., 1982; Van Ranst and De Coninck, 1983; Nash et al., 1988; Fanning et al., 1989; Pestitschek et al., 2012; Skiba et al., 2014). Research carried out in podzolic soils developed from glauconitic sands in Belgium and Wisconsin, USA, showed that weathered glauconite was depleted in Fe^{2+} and K^+ , and enriched in swelling layers relative to unweathered pellets of glauconite (Wurman, 1960; Cloos et al., 1961). Courbe et al. (1981) and Skiba et al. (2014) in the studies focused on soils of temperate climate, described transformation of glauconites directly into smectites. Transformation into smectite was also reported in the studies of weathering of glauconite in warm desert climate (Pestitschek et al., 2012). Abudelgawad et al. (1975) and El-Amamy et al. (1982) studying the weathering in laboratory experiments observed transformation of glauconites (due to charge reduction) into a vermiculites. Hutcheson and Haney (1963) and Nash et al. (1988) documented transformation of glauconites into smectites via vermiculites taking place in soil profiles in humid subtropical climate. Robert (1973) reported similar transformation sequence of glauconite occurring after experimental potassium extraction and iron oxidation. Kaolinite and/or iron oxy/hydroxides have also been reported as products of glauconite weathering taking place in variety of soils and climates (Wurman, 1960; Cloos et al., 1961; Wolff, 1967; Courbe et al., 1981; Loveland, 1981; Nash et al., 1988). Most of the available papers did not provide a comprehensive description of the studied environments nor a detailed characteristic of primary glauconite (Skiba et al., 2014 and literature cited therein). Most of the studies were focused on acidic environments therefore little is known about weathering of glauconite in more alkaline conditions.

Glauconite is a main constituent of so called greensands, which are commonly used in agriculture as effective “organic” (i.e. natural) fertilizers and soil conditioners. Because of the structure instability in soil environment glauconite constitutes a source of potassium and iron, which are easily uptaken by plants. The main advantages of greensands over traditional KCl-based fertilizers lies in the fact that application of glauconite does not cause neither groundwater and soil salinization nor an uptake of heavy metals (e.g. Cd) by the plants, (Zhao et al., 2003; Franzosi et al., 2014). Additionally due to a much lower relative to KCl solubility of glauconite greensands constitute a stable and long lasting source of potassium. Application of greensands also prevents potassium from being leached out from soils. Because of those reasons mechanism of glauconite weathering is of great interest. The aim of the present work was to study the weathering of glauconite in an alkaline environment which took place most likely during Paleogene within regolith developed on Cretaceous glauconite-marls in Zabierzów (Southern Poland).

2. Materials and methods

Samples used in the present study were collected in an abandoned limestone quarry in Zabierzów (Krakow area) (50°6'50" N 19°47'15" E).

The quarry is located on the northern edge of Tenczynek horst (Fig. 1). In the quarry series of normal faults cutting Jurassic and Cretaceous rock complex were reported (Gradziński, 1962; Felisiak, 1992) with the major fault dividing the quarry into two blocks (Fig. 1). One block was uplifted relative to the other one and due to erosion the Santonian glauconite-bearing marls were uncovered and underwent weathering, whereas in the other block the same marls were preserved in their initial state. Fresh (i.e. unweathered) glauconite-bearing marls (sample GC41) were sampled in the lower part of the quarry where they were excavated during a construction work. A regolith profile developed on the glauconite-bearing marls most likely in Paleogene (Felisiak, 1992; Kowalski, 1986) was sampled in the upper part of the quarry. Three horizons were distinguished within the regolith profile: the lowermost moderate olive brown horizon (sample GC19), the middle pale reddish brown horizon (sample GC20), and the uppermost dark yellowish orange one (sample GC21) (Fig. 2, Table 1). In all of these horizons green, glauconite pellets were clearly visible. The term “regolith” is used here since only remnants of the original soil profile are now available. One can only speculate that the original soil could represent soil type commonly described as “terra rossa/red rendzinas”. Samples used in the present study were collected from the material which could be regarded as C and BC horizons of the paleosol profile.

Thin sections were prepared from undisturbed samples and studied under optical microscope. Bulk samples were air-dried, pre-ground and passed through 0.4 mm sieve. Samples pH was measured in de-ionized water (1:1sample:water ratio).

Quantitative mineral composition was determined for the bulk samples using Rietveld method. The calculation were performed with the Rietveld AutoQuan/BGMN computer program (Taut et al., 1998). Clay fractions ($< 2 \mu\text{m}$ and $< 0.2 \mu\text{m}$) were separated from bulk samples by centrifugation proceeded by simplified Jackson's (1969) procedure. Glauconite (green pellets) were separated from sand fractions using neodymium bar magnet. The separated clay fractions were saturated with Mg^{2+} , K^+ and Ca^{2+} and the green pellets were ground and saturated with Ca^{2+} . Oriented mounts were prepared by deposition of the material dispersed in de-ionized water on glass slides. Random mounts were prepared for Mg-saturated fine clay fractions and for pellets separated from GC41 and GC19 samples. XDR patterns of K-saturated and Mg-saturated clays were collected in air-dry conditions at ambient relative humidity (27.5–47%). K-saturated clays were also analyzed after heating the mounts for 1 h at 330 °C and at 550 °C while Mg-saturated clay fractions were analyzed after solvation with liquid glycerol (GS). Ca-saturated fine clays and pellets were analyzed in air-dried conditions and after solvation the mounts with ethylene-glycol vapours (EG). To compare the studied glauconites between each other regarding the concentration of expandable layers, Intensity Ratios (IR) were calculated for Ca-saturated fine clays and pellets, according to formula given by Śrdoń (1984).

Mg-saturated fine clay ($< 0.2 \mu\text{m}$) fractions separated from all studied samples and pellets separated from parent marls (samples GC19 and GC41) were analyzed using Fourier transform infrared spectroscopy (FTIR) in forms of KBr pressed discs. Obtained spectra were analyzed in detail in ranges of $3000\text{--}3800 \text{ cm}^{-1}$ (OH-stretching region). Decomposition of the spectra was performed and individual bands were identified based on frequencies given by Besson and Drits (1997). Mössbauer spectroscopy was used for determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in glauconites separated from the least weathered samples (GC41 and GC19). Scanning electron microscope fitted with energy dispersive X-ray spectroscopy was used for observation of morphology of glauconite pellets and chemical analysis of separated unweathered pellets and the weathering products in thin sections. Chemical formulas of glauconite were calculated from average chemical composition based

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