



Native alunogen: A Raman spectroscopic study of a well-described specimen

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ABSTRACT

Alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) is a common secondary mineral in the terrestrial environment (acid mine drainage, volcanic or coal-fire fumaroles), and is also formed through the acidic weathering of aluminosilicates. Moreover, alunogen has been suggested as a part of the Al-bearing deposits on Mars. The identification of alunogen in secondary sulfate mixtures by Raman spectroscopy strictly depends on good knowledge of alunogen spectral features and band positions. However, comprehensive Raman data of alunogen of natural origin are lacking. This study reports on Raman spectra obtained from two natural specimens originating from a burning coal dump at the Schoeller mine, Kladno, Czech Republic, along with the additional characterizations by infrared spectroscopy, X-ray diffraction, and electron microprobe. For comparison purposes, a Raman spectrum of a synthetic analogue was also obtained. The studied specimens have $(\text{Al}_{1.99}\text{Fe}^{3+}_{0.01})_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ as their calculated empirical formula, and the structural parameters correspond to the previously reported data for alunogen. Both natural specimens and the synthetic analogue showed uniform Raman spectra with no extensive band splitting in the sulfate vibrational regions. The most intensive Raman band associated with the symmetric stretching vibration of the SO_4 tetrahedra (ν_1) is located at 992 cm^{-1} . A multicomponent band was observable in the characteristic region for OH-related vibrations. A small variation in the spectral intensity of the hydroxyl bands suggests that the studied specimens could possibly be slightly dehydrated.

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1. Introduction

Secondary aluminum sulfate minerals are very common products of the decomposition of aluminosilicate minerals (mostly feldspars, micas, or clay minerals). They frequently precipitate from solution under low pH conditions with a high presence of sulfate anions. These minerals are found in efflorescences associated with acid mine drainage phenomena [1], in secondary encrustations of volcanic fumaroles [2,3], or as components of corrosion crusts in caves with the presence of H_2S thermal springs [4]. Aluminum and even ammonium-aluminum sulfates frequently occur as alteration products of waste rocks at burning coal waste dumps [5–8].

Moreover, hydrous sulfate minerals have played an important role in the Martian aqueous history, and may act as paleoclimatic and geochemical indicators, as well. So far, Ca-, Mg-, and Fe-sulfates

have been detected on Mars from both orbital and surface data [9–14]. Aluminum sulfates are significantly rarer, and they have only been found in the form of alunite in the Cross crater of the Terra Sirenum region [15,16]. However, Al-enriched deposits have been detected in many regions of Mars [12]. These deposits may be a result of the extensive weathering of Martian basaltic rocks under specific acid conditions, as certain models have suggested [17,18]. Based on experimental weathering of Martian basalt analogues, silica and Al-containing sulfates, including alunogen, are believed to be among Al-enriched products of acidic weathering of basaltic glass [17,19].

Alunogen is a simple aluminum sulfate, featuring a very high water content, and has the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$. Alunogen crystallizes in the triclinic space group $P\bar{1}$; however, a low-temperature modification (monoclinic, space group $P2_1$) can also exist [20]. The alunogen structure is based on sheets of isolated $\text{Al}(\text{O}_w)_6$ octahedra and SO_4 tetrahedra which are interconnected via a network of hydrogen bonds. The water molecules occupy two

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different kinds of sites. They either behave as ligands, where oxygen is bound to one Al atom and acts as a proton donor to a sulfate oxygen, or they lie in channels running parallel to [001]. These sites are usually termed as “free” or “zeolitic” water. Fang and Robinson [21] determined the maximum water content of alunogen to be 17 molecules. However, alunogen crystals exposed to low humidity are vulnerable to dehydration. Therefore, the occupancy of one “free” water site is often partial and thus the real amount of water is less, probably between 16 and 17 water molecules per formula unit [21,22]. Under very low humidity (lower than 20%), there is a very distinctive loss of water of about 2 mol of water per mol $\text{Al}_2(\text{SO}_4)_3$, resulting in the lower hydrated 13.7-hydrate corresponding to meta-alunogen [23].

Raman spectroscopy has proven very useful for the study of various sulfates, including those containing aluminum [24–26]. In the last decade, progress in the miniaturization of Raman spectrometers has allowed for the *in situ* detection and identification of sulfates [27–31]. A detailed Raman spectroscopic study of secondary minerals is necessary for the interpretation of natural mineral mixtures. However, previous Raman studies have only involved the use of a synthetic analogue of alunogen [20,32] or natural mixtures of more complicated composition [33].

In this work, we use Raman spectroscopy to study for the first time two natural alunogen specimens from a burning coal waste dump at Kladno. These specimens are part of a reference mineral collection from these “exotic” settings, and samples are available for further studies. We also compared the obtained Raman spectra with the Raman spectrum of a synthetic analogue. Due to their origin, the investigated alunogen samples contain impurities; therefore, detailed powder X-ray diffraction analysis (PXRD), electron microprobe analysis (EMPA), and infrared spectroscopy (IR) were carried out for closer structural and chemical descriptions of the investigated samples.

2. Materials and methods

2.1. Samples

Both of the studied samples of native alunogen were collected on the new waste dump of the former Schoeller or Nejedlý I coal mine (1899–2002) at Kladno, Czech Republic. They formed during the long period of spontaneous combustion of residual coal in the waste dump at the so-called Fumarole N°1 (50.1691°N, 14.0342°E; see Záček and Skála [7]), at a temperature of about 30–50 °C. The long-term activity of this fumarole led to the formation of a large “sulfate cup” (up to ca. 50 cm thick), with dominant Al-sulfates such as millosevichite, godovikovite, alunogen, khademite, and tschermigite [34]. This locality was studied until 2002 when it ceased to exist due to restoration work on the dump [7].

Sample K159 was collected in February of 1995 from a massive sulfate crust from 5 to 10 cm below the surface, and was a chip $5 \times 3 \times 1.5$ cm in the size that was white, in part yellowish, with a sugary and fine crystalline structure. Sample K301 was collected in November of 1986 from a cavity 10–15 cm below the surface. It is a stalactite $6 \times 2 \times 1$ cm in size, whitish to yellowish in color, hard, with a crystalline internal structure, and the surface covered with a fine white fibrous mineral. The materials for the instrumental study (grains of 1–3 mm) were separated under a binocular microscope (see Fig. 1).

The synthetic crystalline aluminum sulfate (declared as $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), for comparisons of the infrared and Raman spectra obtained, was supplied by Penta (Prague, Czech Republic).

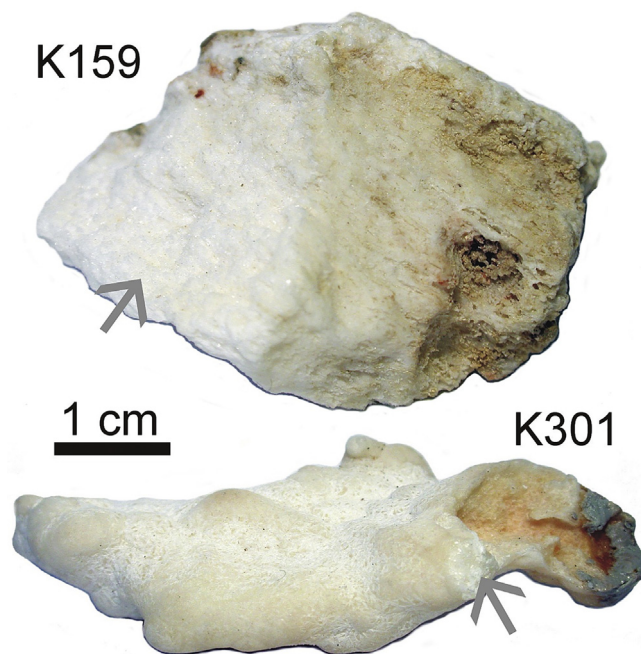


Fig. 1. Studied specimens of alunogen collected on the waste dump of the former coal mine Schoeller or Nejedlý I at Kladno, Czech Republic.

2.2. PXRD

The powder X-ray diffraction data for both samples were collected in the Bragg-Brentano geometry on a Bruker D8 Advance diffractometer, equipped with a Lynx Eye XE detector and Soller slits (2.5°) in the primary and secondary beams. $\text{CuK}\alpha$ radiation was used. The samples were gently pulverized together with acetone in an agate mortar. To minimize the background, the sample was placed on a flat silicon wafer from the acetone suspension. The diffraction data were collected within the angular range of 4–80° of 2θ with a step of 0.015°, and 0.6s counting time per step. An automatic divergence slit (10 mm) was used. The qualitative phase analysis was performed using the DIFFRAC.Eva (Bruker AXS 2015) program and the PDF-2 database (ICDD 2002).

The unit-cell parameters were calculated *via* the Rietveld method using the Topas 5 (Bruker AXS, 2014) program. The initial structural model for alunogen was adopted from the work of Fang and Robinson [22]. During the refinement, only the unit-cell parameters, crystal size, and correction for the preferred orientation along [010] were refined. The structural model of Fang and Robinson [22] was confirmed.

2.3. Electron microprobe

A carbon-coated polished section of several grains was used in the study using an electron microprobe. Chemical microanalyses were performed with a Cameca SX-100 electron microprobe (Joint laboratory of Masaryk University and the Czech Geological Survey, Brno, Czech Republic) operating in the wavelength dispersion mode, with an accelerating voltage of 15 kV, a sample current of 10 nA, and a beam diameter of 10 μm . The $K\alpha$ lines and following standards were used: Si, Al, K - sanidine; Na - albite; Mg - Mg_2SiO_4 ; Fe - almandine; Mn - spessartine; S - SrSO_4 ; Ca, P - fluorapatite; F - topaz; and Cl - vanadinite. The raw data were converted into the concentration using the X-PHI matrix correction [35]. The water content, calculated as the deficiency compared to 100 wt% of the analytical total was figured into the matrix corrections.

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