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KRAUSHÖHLE (AUSTRIA): MORPHOLOGY AND MINERALOGY OF AN ALPINE SULFURIC ACID CAVE

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Kraushöhle (Gams, Styria, Austria) is the only currently known sulfuric acid cave in the Eastern Alps. Cupolas, ceiling partings and portals, ceiling channels, replacement pockets, horizontal corrosion/convection notches, sulfuric acid karren, blind chimneys, incomplete dissolution walls, drip holes and cup shaped hollows in the floor are the most striking morphological features in this cave. Mineralogical analysis showed the presence, besides calcite, of gypsum, gibbsite, opaline, jarosite, metalunogene, hydroxylapatite, halloysite, and alunite. The timing of speleogenesis was preliminarily determined using $^{40}Ar/^{39}Ar$ dating of alunite, a product of acid limestone weathering, to 80 Ka +/- 80 (the cave is thus younger than 160 Ka). Preliminary U-Th dates of calcitic stalagmites indicate a minimum age of gypsum deposition of 52 Ka. Stable isotope data of these speleothem are consistent with an epigenic origin of the drip water at that time.

1. Introduction

Sulfuric acid corrosion in caves was first identified in France (Socquet, 1801), then in Austria and Italy (Hauer, 1885; Principi, 1931; Martel, 1935). Sulfuric speleogenesis was discussed later in the American literature (Morehouse, 1968). The remarkable publication on Kane Cave (USA) by Egemeier (1981) suggested a speleogenesis entirely dependent on the effect of sulfuric vapor, which caused the replacement of limestone by gypsum. This cave, at that time considered to be an "exotic" form of speleogenesis, became a reference work after the discovery of the famous Lechuguilla Cave in New Mexico (Hill, 1987; Hose et al., 2000; Engel et al., 2004). Considerable progress with regard to gypsum development and corrosion was made in Italy, mainly by the study of the Frasassi caves (Galdenzi and Menichetti, 1995). Following Egemeier, Audra et al. (2007) suggested that a major part of sulfuric speleogenesis may occur in the cave atmosphere (i.e., above the water table) by thermal convection and condensation-corrosion.

The sulfuric acid process of speleogenesis is based on the oxidation of sulfides to sulfuric acid (1), either directly, or by an intermediate reaction involving native sulfur (2). These reactions are facilitated by sulfo-oxidant microbes. Sulfuric acid then reacts by dissolving the calcareous host rock, creating replacement gypsum and releasing carbon dioxide (3), which dissolves even more limestone according to the reaction (4):

(1) $H_2S + 2O_2 <=> H_2SO_4$ ($SO_4^{--} + 2H^+$ in aqueous solution)

(2) $H_2S + O_2 => 2S° + H_2O$ and $2S° + 3O_2 + 2H_2O => 2 SO_4^{--} + 2H^+$ (in aqueous solution)

(3) $CaCO_3 + SO_4^{--} + 2H^+ + 2H_2O => CaSO_4 \cdot 2H_2O$ (gypsum)′ $+ CO_2' + H_2O$

(4) $CaCO_3 + CO_2 + H_2O => Ca^{++} + 2HCO_3^-$

The general reaction of sulfide oxidation thus requires oxygen in gaseous or dissolved form. Limestone undergoes a double dissolution, part involving the replacement by gypsum. Dissolved sulfate and alkalinity are carried away by the karst water. The reactive paths of the sulfuric replacement corrosion develop from the deeper, phreatic parts of the aquifer to the vadose zone near the emergence according to the following succession:

- At depth in the aquifer: microbial reduction of sulfates derived from evaporites into sulfites;

- in the aquifer body: possible addition of sulfate derived from the oxidation of pyrite, likely to be re-reduced thereafter;

- at shallow depth: dissolved sulfide of deep water partly becomes oxidized by mixing with oxygenated meteoric water, reacts with the limestone rock and produces sulfate in solution.

- In the confined atmosphere of the cave: H_2S degasses and oxidation continues, forming sulfuric acid on the walls and in the cave pools: sulfuric acid dissolves limestone, which is replaced by gypsum.

- Above the water table: condensation runoff along the walls dissolves gypsum. The detachment of the gypsum crusts makes them fall into the pools and adds to the washing out of sulfates;

- In the pools: the slowly flowing water gradually removes alkalinity and sulfate produced by the sulfuric dissolution of limestone.

In this paper the results of a multidisciplinary study on a remarkable sulfuric acid cave in the Eastern Alps, Kraushöhle near Gams in Styria (Austria) are reported.

2. Exploration History and Previous Works

Franz Kraus started exploration of a small and inconspicuous cave ("Annerlbauerloch") in 1881 and discovered most parts of Kraushöhle as it is known today. Due to rich speleothem decoration, but primarily because of massive gypsum deposits, he excavated a second entrance and opened "Kraus-Grotte" for visitors as early as 1882. In 1883 Kraushöhle became the first show cave in the world equipped with electric lights – one year before Postojnska Jama. Hauer (1885) already linked cave genesis to a nearby sulfide spring and suggested replacement of limestone by gypsum as a minor cave-forming process. Kraus (1891, 1894) supported this hypothesis ("cave genesis due to metamorphism") and gave a detailed description of the cave and its morphology. Trimmel (1964) interpreted the origin of the *Main Chamber* by dissolution of a gypsum body. Puchelt and Blum (1989) examined the sulphur isotopic composition and validated the hypothesis of Hauer (1885), but also concluded that this process had only limited impact on the development of the cave. No detailed morphological studies had been carried out on this cave prior to our study.

3. Study Site

Kraushöhle is situated in the easternmost section of the Hochschwab karst massif which is part of the Northern Calcareous Alps (NCA). The area shows a complex tectonic style and is affected by major strike-slip faults. Whereas the NCA are dominated by Triassic carbonates the cave formed in the Hirlatz Formation, a red Jurassic crinoidal limestone. The cave opens at 616 m asl, 90 m above the Gams brook that carved a narrow gorge in its upstream section. According to a complete resurvey in 2008 the total length of the cave is 767 m and the vertical range is ±53 m (+31, −22 m; Fig. 1). The cave consists of a *Main chamber* 50 m long, 6 to 15 m wide, and a volume of ca. 6000 m^3. It is connected with another chamber, the *Elysium* (25 x 10 m). Several conduits spread from these chambers that are partly parallel and interconnected. They are mainly subhorizontal but also show vertical steps of up to 10 m. Both cave entrances are incidental intersections of the cavern with the erosion surface. The section close to the upper entrance shows a 3D maze pattern (Fig. 1). Several blind chimneys up to 4 m in diameter reach upward; the highest of them terminates 30 m above the floor of the main chamber. A step of this chimney, which is not covered by gypsum or clastic sediments like most of the other parts of the cave floor, shows up to 1 m deep karren. The walls and the ceilings of almost all parts of the cave are formed by cupolas and mega-scallops. Larger cupolas have diameters of up to 3 m and often show portals that connect two of them. Notches with flat roofs and convection niches formed at several levels, in particular in the *Main chamber*. Condensation-corrosion channels are mainly present close to the lower entrance. Especially the lower parts of the cupolas are sculptured by gypsum replacement pockets.
In the southernmost gallery several cup-shaped corrosion features are present below triple junctions of cupolas. Both chambers, the interconnected galleries east of them and adjacent chimneys contain gypsum. Massive gypsum on the floor is up to a few meters thick and is often perforated by drip holes. On the walls and ceilings gypsum crusts and crystals are present, which reach up to 30 cm in length in the main chimney where they cover several square meters. The cave also contains calcite speleothems including stalagmites, helictites, popcorn, a shield and locally extensive moonmilk.

During strong rain or snowmelt several small rivulets enter the cave. Water drains towards the deepest point of the cave which is blocked by breakdown material. Parts of the cave that are affected by this modern vadose water lack gypsum deposits. Locally this epigenic overprinting is documented by allochtonous pebbles that are typical for the geological units in the upstream part of Gams Brook. A lukewarm H_2S-rich spring (8.6 - 20.0°C) emerges at the level of the Gams Brook, 71 m below the deepest known point of the cave. Isotope data show that the water is a mixture of cold karstic and thermal waters (Zetinigg, 1993). Presently there is no thermal anomaly in Kraushöhle. The average annual temperature in the *Main chamber* is 7.6 (±0.2) °C which corresponds perfectly with the average outside air temperature.

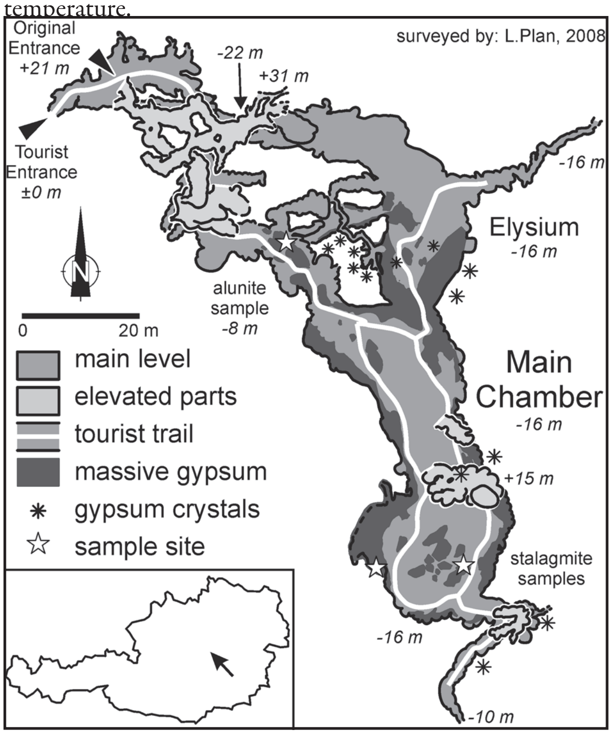

Figure 1: *Plan view of Kraushöhle with gypsum occurrences, sample sites and location in Austria.*

4. Morphologies and Their Genesis

The morphology of the cave is mainly due to its sulfuric origin by H_2S degassing of water rising from depth. H_2S oxidized to sulfuric acid either in shallow pools fed by both rising water and downflowing condensation runoff, or on walls and ceilings through condensation. These two types of environments (i.e. aqueous/gaseous) produced two families of corrosion features. The sulfuric water probably ascended along fractures, which are no longer visible due to later clay deposition. In the *Main chamber* and in some adjacent passages shallow pools were present. The aggressive water body caused lateral corrosion, which formed a notch with a flat roof, corresponding to the former pool level (Fig. 2A). The rising water was also probably thermal. At the rim of the "warm" pools, juxtaposed convection cells caused condensation-corrosion (Fig. 2B. Wall convection niches developed, which intersect in a blunted vertical edge (Fig. 2C). When deeply incised into the wall, their coalescence tends to form a notch with shallow embedded niches (Fig. 2B). The thermal gradient produced convection cells of bigger size, which carved the upper walls and the ceilings according to the airflow paths. Condensation-corrosion produced wall niches, ceiling cupolas (Fig. 2H), condensation-corrosion channels, and blind chimneys, whose walls are covered by megascallops (Fig. 2G). As a consequence, and in contrast to epigenic caves which develop along the entire conduit length, sulfuric caves developing mainly by condensation-corrosion, expand at discrete places (Osborne, 2007). Adjacent passages intersect, creating larger passages which evolve into condensation domes. Remnants of wall partings form ceiling partings, portals (Fig. 2H), protruding corners, blades, etc. Condensation prevailed in the "cool" upper parts, causing diffuse and differential corrosion and giving rise to boxwork-like structures. On the contrary, the lowest parts of the walls were warmer and prone to evaporation. Sulfate precipitated as gypsum crusts, giving rise to corrosion below the gypsum deposits. At half-height of the wall, where condensation and evaporation competed, gypsum is restricted to replacement pockets (Galdenzi and Maruoka, 2003) (Fig. 2D). Downwards, gypsum crusts thickened as a result of increasing evaporation. These crusts commonly detached from the walls and piled up as gypsum floors, locally in excess of 1 m (Fig. 2E). Primary formation of gypsum occurred as microcrystalline gypsum, and later recrystallization through condensation and evaporation produced large crystals (Fig. 2F). Calcite speleothems did not form during the hypogean phase, and are most likely entirely related to the epigene phase. After the cessation of the sulfuric phase, morphological changes due to meteoric infiltrations also resulted in the deposition of clay. Consequently, diagnostic features of hypogenic speleogenesis such as the "morphologic suite of rising flow" (Klimchouk, 2007) are not clearly visible, being masked by sediments and speleothems.

5. Mineralogy

Thirty samples were taken at different locations inside Kraushöhle. Mineralogical analyses were carried out using a Philips PW 1050/25 X-ray diffractometer, and, if only small amounts of sample were available, using a Gandolfi chamber (diameter 114.6 mm). In both cases the

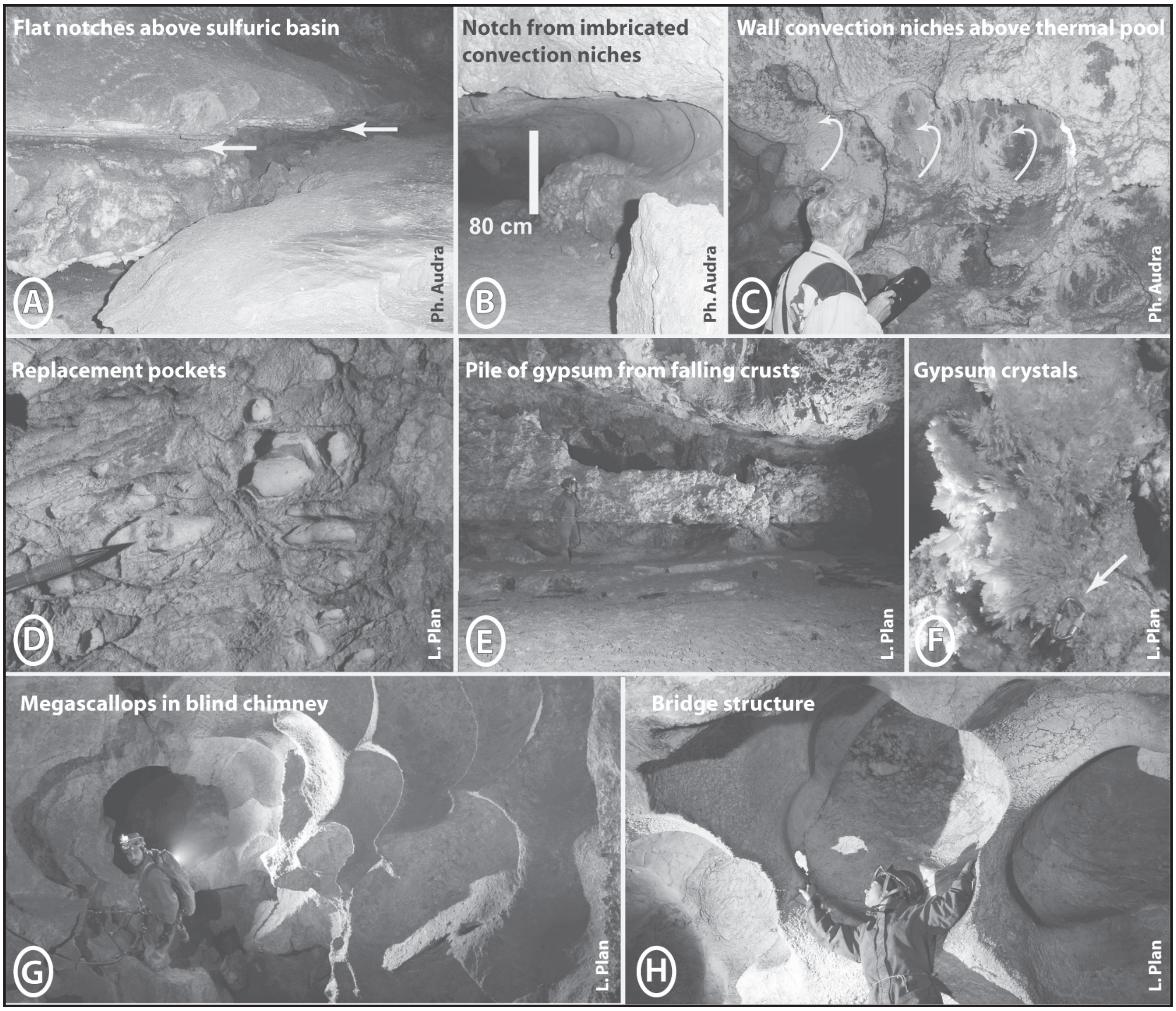

Figure 2: *Cave morphologies: A) Notches with flat roofs carved by lateral corrosion of a sulfuric acid pool; B) Notch formed by imbricated wall convection niches above the level of the thermal basin; C) Wall convection niches above the thermal pool; D) Replacement pockets; E) Pile of gypsum from detaching crusts; F) Gypsum crystals; G) Megascallops in a blind chimney; H) Portal between two adjacent cupola.*

experimental conditions included 40 kV and 20 mA, CuKα radiation, and a Ni filter. In addition to calcite (derived from the host limestone) and gypsum, seven additional minerals were identified: opaline ($SiO_2 \cdot xH_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), gibbsite ($Al(OH)_3$), metalunogene ($Al_2(SO_4)_3 \cdot 12H_2O$), halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$), alunite ($KAl_3(SO_4)_3(OH)_6$), and hydroxylapatite ($Ca_5(PO_4)_3(OH)$). Gypsum is abundant in Kraushöhle and forms large deposits or replacement pockets along the walls and on the roofs. Many of the replacement pockets still host the pseudomorph gypsum which preserved structures of the original limestone such as calcite veins and fossils. Opaline is a rather common mineral in lava caves, but is rare in limestone caves (Hill and Forti, 1997). Its presence indicates rather acid conditions, compatible with sulfuric acid speleogenesis. The three sulfate minerals (jarosite, metalunogene and alunite) and the silicate halloysite are also typical of such low-pH conditions and this mineral association has been reported from Frasassi Cave (Bertolani et al., 1973) and from Guadalupe Mountain caves, New Mexico (Polyak and Güven, 1996). These minerals, together with the alluminium hydroxide gibbsite, are the products of alteration of clay deposits under acidic conditions (Polyak and Güven, 1996; De Waele et al., 2008). Hydroxylapatite was found in one single sample only and appears as transparent vitrous inclusions together with minor quartz, illite and gibbsite in a amorphous brown matrix. Its presence might be related to the alteration of organic material (bone?).

6. Alunite

Alunite was reported as a speleogenetic mineral in caves of the Guadalupe Mountains by Polyak et al. (1998) who successfully dated this mineral to yield the timing of speleogenesis of sulfuric acid caves in that area. The raw alunite-bearing Kraushöhle sample was treated with 25% HF for one hour. Approximately half of the raw sample dissolved. XRD results showed the presence of gibbsite in the raw sample, but probably not enough to make up half of the sample. EDS showed the presence of Al, S and K (Fig. 3A). It is likely that amorphous materials make up some of the raw sample. The Kraushöhle alunite crystals are similar in size and appearance to alunite from Carlsbad Cavern and Lechuguilla Caves (Polyak et al., 1998; Polyak and Provencio, 2000). They are pseudo-cubic rhombs ranging in size from 1-10 µm (Fig. 3B). After HF treatment, XRD results showed pure alunite (Fig. 3C). Refined unit-cell dimensions of A = 6.962 Å and C = 17.260 Å indicate that the sample consists of K-rich, near-end-member alunite.

The speleogenetic Kraushöhle alunite has an exceptionally young $^{40}Ar/^{39}Ar$ plateau age (≤160 ka), suggesting that the timing of formation of the cave is recent (Fig. 4). This is the first dated cave alunite outside of the Guadalupe Mountains.

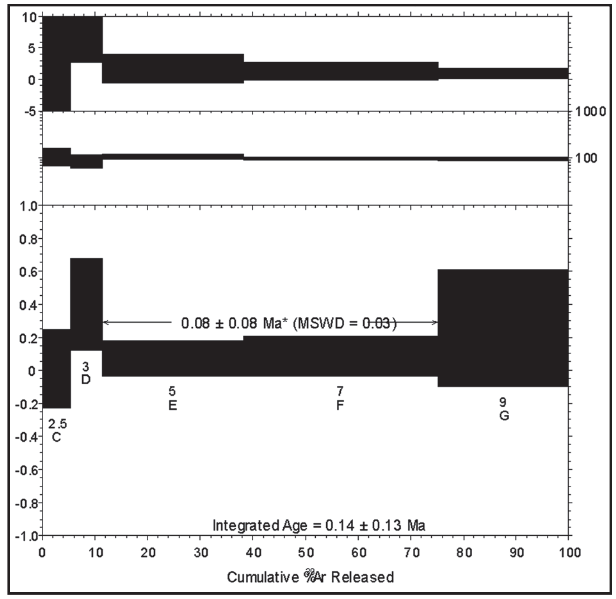

Figure 4: *$^{40}Ar/^{39}Ar$ age spectrum for a sample of fine-grained alunite from Kraushöhle, Austria.*

7. Calcite Speleothems

Kraushöhle contains abundant stalagmites, many of which were removed by vandalism. Preliminary investigations suggest that these speleothems are low-Mg calcite and

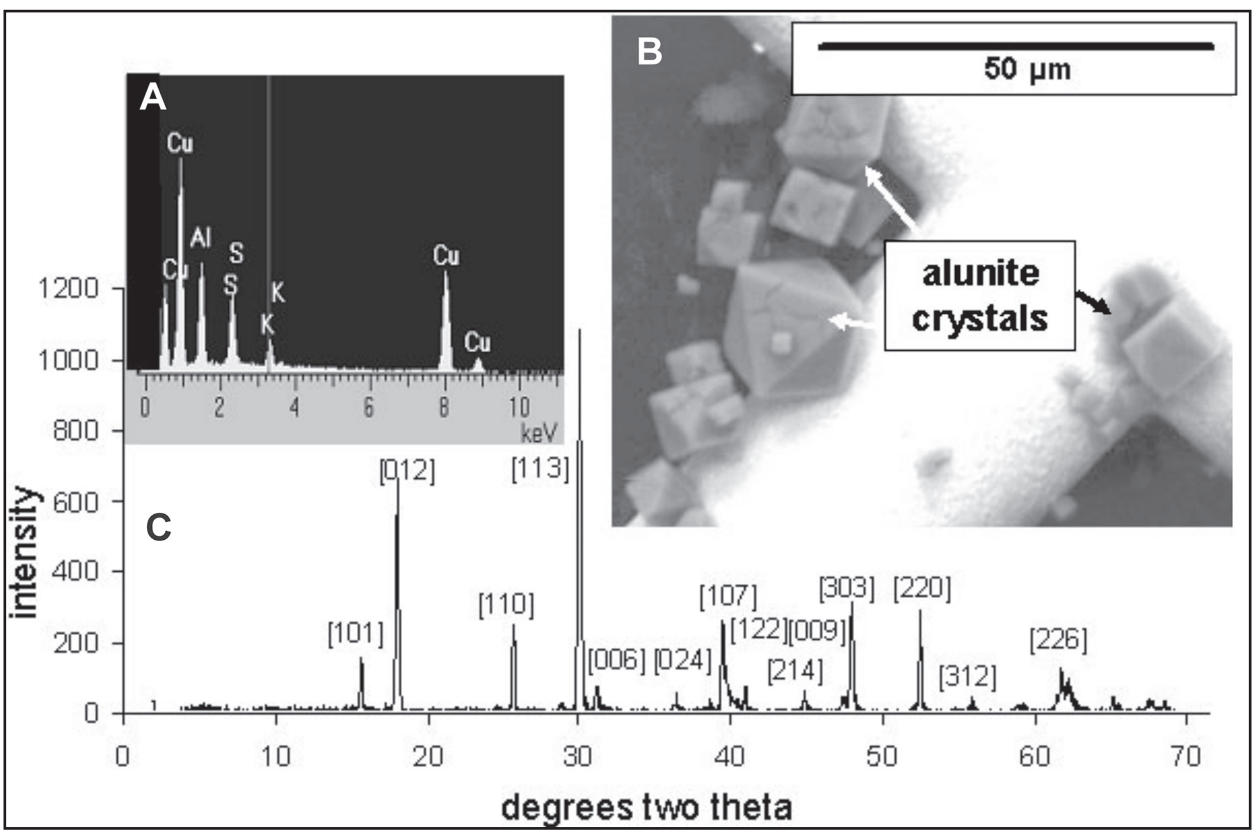

Figure 3: The Kraushöhle alunite is the K-rich endmember. A) the three detectable elements using EDS are Al, S, and K; B) crystals are micron-sized rhombs; C) the XRD pattern of the HF-treated aliquot indicates that alunite is the only crystalline phase.

are composed of a dense, transparent fabric. Speleothem deposition clearly postdated formation and local subsequent dissolution of massive gypsum as shown by the location of stalagmites in depressions surrounded by remnants of thick gypsum. Active soda straws and flowstone crusts on roots (close to the upper entrance) give evidence of rapid modern speleothem and moonmilk formation.

Fragments of two inactive stalagmites were dated using U-Th methods and yielded ages of 52 and 36 ka, thus providing a minimum age constraint for the cessation of gypsum deposition and subsequent local removal. $\delta^{13}C$ values range from -7.9 to -6.9‰ and from -2.4 to +0.4‰ VPDB suggesting variable amount of biogenic (soil-derived) C input into the seepage waters during this early stage of epigenic speleogenesis. $\delta^{18}O$ values range from -8.6 to -8.2‰ and from -10.3 to -8.5‰ VPDB. Modern drip water samples are required to relate these values to past environmental conditions, but it is likely that the large range in O isotope values of the second sample represents a paleoclimatic signal, consistent with the known high-amplitude climate variability during the time interval of the last glacial.

8. Conclusions

Kraushöhle is a remarkably young sulfuric acid cave with a minor epigene overprinting. The suite of morphologies such as cupolas, ceiling partings and portals, ceiling channels, replacement pockets, horizontal corrosion/convection notches, sulfuric acid karren, blind chimneys, incomplete dissolution walls, drip holes and cup-shaped hollows in the floor are diagnostic features of hypogenic speleogenesis due to sulfuric acid. Also mineralogy displays a distinctive set of sulfates and hydroxides typical of acid weathering. Alunite, in particular, has been dated using the $^{40}Ar/^{39}Ar$ method and has shown that the acid corrosion, responsible for the cave development, is younger than 160 ka. Two U/Th dated stalagmites yielded ages of 52 and 36 ka and confirm the extremely young epigenic phase that followed the sulfuric acid speleogenesis.

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