### NITROCALCITE IN KARTCHNER CAVERNS, KARTCHNER CAVERNS STATE PARK, ARIZONA, USA

NITROKALCIT V KARTCHNERSKIH JAMAH, NARODNI PARK KARTCHNERSKIH JAM, ARIZONA, ZDA

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#### Abstract

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# Hill, Carol A. & Robert H. Buecher: Nitrocalcite in Kartchner caverns, State Park Kartchner caverns, Arizona, USA

Nitrocalcite  $(Ca(NO_s)_2.4H_2O)$  is a deliquescent mineral, afflorescent only under very low humidity conditions. Brief mention of nitrocalcite as a cave mineral has been given for one cave in the southwestern United States and one cave in Italy. Nitrocalcite occurs in Kartchner Caverns as a cave cotton growing from sediment in scattered areas along the Entrance Passage where cold, dry, winter air flows into the Entrance Passage from the surface. The present article is the first authenticated, detailed description of nitrocalcite as a cave mineral.

Key words: cave mineral, nitrocalcite, Kartchner Caverns, United States of Amerika

Izvleček

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Nitrokleit (Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O) je topljiv mineral, ki se pojavlja samo v zelo vlažnih pogojih. Bežna omemba nitrokaleita kot jamskega minerala je znana le za eno jamo v jugozahodnih Združenih državah Amerike in za eno jamo v Italiji. Nitrokaleit se pojavlja v Kartchner Caverns v obliki "jamskega bombaža" na sedimentih na nekaterih mestih vhodnega rova, kjer pozimi mrzel in suh zrak priteka vanj s površja. Pričujoči članek je prvi avtentični natančni opis nitrokaleita kot jamskega minerala.

Ključne besede: jamski mineral, nitrokalcit, Kartchner Caverns, ZDA

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Nitrocalcite (Ca(NO<sub>3</sub>)<sub>2</sub>µ4H<sub>2</sub>O) is a deliquescent mineral, efflorescent only under very low humidity conditions (around 50% for a normal range of cave temperatures; HILL & FORTI, 1986; Figure 1). Nitrocalcite has been mentioned as occuring in a number of eastern United States caves, but these are pre-1900 citings which are erroneous since eastern caves have relative humidities approaching 100%. Brief mention of nitrocalcite as a cave mineral has been given for one cave in the southwestern United States and one cave in Italy (HILL & FORTI, 1986). This is the first authenticated, detailed description of nitrocalcite as a cave mineral.

Nitrocalcite occurs in Kartchner Caverns as cave cotton growing from sediment in scattered areas along the Entrance Passage (e. g., Babbitt Hole and LEM Room, Figure 2) where cold, dry, winter air flows into the Entrance Passage from the surface. Mineralization occurs as efflorescent cotton mats, consisting of colourless to milky-white, silky-to-transparent, slender needle crystals up to 0,5 mm in length and <0,1 mm in width (Figure 3). Birefringence is high: third order yellows, pinks and greens. One optical indice measured <1,50, another >1,50. Some of the needle crystals look eaten-away along their edges and many have a thin coating of clay on their surfaces. The mineral has a strong, bitter-cool taste.

Nitrocalcite was positively identified by D. Bish of Los Alamos Laboratory using X-ray diffraction techniques. A composite powder of the cotton material exhibits peaks for calcium nitrate hydrate (not a named, naturally-occurring mineral species), calcite, and quartz; in addition, a possible peak for a clay mineral was detected. The calcite is probably normal secondary mineralization within the sediment, the quartz is probably detrital (tiny pieces of needle quartz in the sediment?), and the clay mineral is probably clay coating the nitrocalcite crystals. It seems probable that the calcium nitrate hydrate (two waters of hydration) is a dehydration product of nitrocalcite (four waters of hydration). The mineral was kept in a closed container containing desiccant since its collection (December, 1989) and the diffractometer was kept below 10% relative humidity during X-ray analysis, so the dehydrated form of nitrocalcite was not unexpected.

The growth of nitrocalcite in the Entrance Passage was monitored by a data logging system which recorded cave temperature and relative humidity on an hourly basis. A weather station was also operated on the surface near the cave entrance. From December 10, 1989 to December 16, 1989 the weather on the surface was unusually dry and cold, with the outside humidity dropping to 23%. The cotton was first noticed on December 14 in front of the Babbitt Hole, two days after the significant drop in surface humidity. Maximum growth was noted on December 12th at Babbitt Hole as a loose mat 1-2 cm thick when the cave humidity and temperature measured 45,3% and

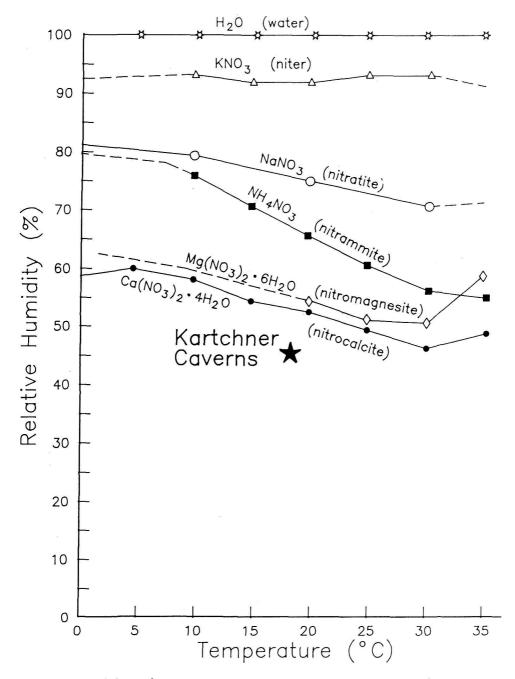


Figure 1. Stability of nitrate minerals in a cave environment with respect to temperature and humidity, showing the Kartchner Caverns nitrocalcite (star) plotted below the nitrocalcite line in the zone of efflorescence. After Hill and Forti (1986).

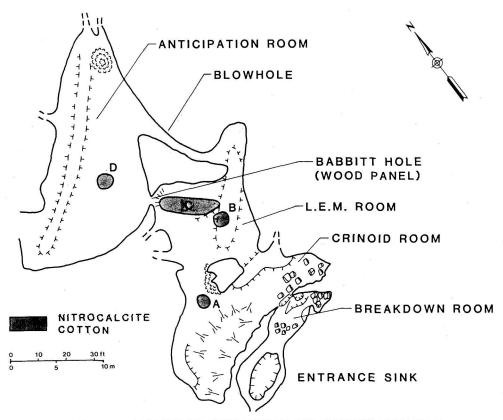


FIGURE 2 LOCATION OF NITROCALCITE IN THE ENTRANCE PASSAGE OF KARTCHNER CAVERNS, DECEMBER, 1989

Figure 2. Location of nitrocalcite in the Entrance Passage, Kartchner Caverns.

15,6 °C, respectively (star, Figure 1). When both surface and cave humidity rose a few days later the nitrocalcite slowly deliquesced and disappeared back into the floor sediment. A humidity of 49–50% or below appears to be needed for crystallization, and the humidity needs to remain low for a few days before significant cotton effloresces. This corresponds to a time when the cave is "breathing in" — that is, when cold, dry air is coming into the cave from the outside. When the cave "breathes out," warm moist cave air quickly causes the mineral to deliquesce and disappear back into the cave sediment.

Interestingly, maximum nitrocalcite growth does not occur in undisturbed dirt off the trail, but it occurs where dry sediment of the Entrance Passage becomes compacted and smeared with mud by crawling cavers returning from the wet, muddy interior of the cave. It may be that, where sediment becomes compacted, nitrocalcite cannot crystallize within sediment pore spaces but must crystallize at the surface of the sediment. It has been noted that crystallization obliterates boot and knee-pad marks in the sediment within a few days time; evidently, sediment particles are forced upward by



Figure 3. An efflorescent mat of nitrocalcite cotton, Entrance Passage. Photo taken on December 14, 1989 by R. Buecher.

cristallization within sediment pore spaces. Scattered patches of dark bat guano can be seen all along the Entrance Passage where the trail has not been crawled over. Cave rat trails can also be seen along the passage walls. Bat and rat guano could both be possible sources of nitrates for the nitrocalcite mineralization.

#### REFERENCES

Hill, C. A., & Forti, P., 1986, Cave Minerals of the World: Huntsville, Alabama, National Speleological Society, 238 p.