

ORIGIN AND DISTRIBUTION OF MINERAL SPECIES IN
LIMESTONE CAVES

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Abstract

More than 80 mineral species are known to result from secondary chemical reactions in solutional limestone caverns. These minerals are transitional and end-products of carbonate wall rock interactions with ground water and organic residue. Bacteria are often critical in fixing various ions in these reactions. Ultimate source of metallic ions is usually the sulphide minerals weathering in overlying strata, and brought to the cave environment by circulating ground waters. Hydrothermal solutions may bring heavy metallic ion concentrations from deeper strata. About one-third of the known cave mineral species occur in stalactitic form.

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INTRODUCTION

Since the Second World War a vigorous scientific interest has focused on the chemical and physical processes active in the cavern environment. The few caves that have been systematically studied were found to contain entirely unsuspected minerals. Further studies on determining the number and distribution of cave minerals will increase our understanding of the bulk composition of mineralising solutions. When one considers the interactions between the carbonate minerals in the wall rock with organic residue or with mineralised ground water, more than 80 mineral species are known. In this paper only minerals that are formed *within* solutional limestone-dolomite caves are considered. These are the result of low temperature and low pressure mineralisation reactions after the formation of the cavernous void itself, thus constituting a secondary process. Detrital mineral grains washed in from outside the cave are not considered in this respect.

The following tabulation of known cave minerals, their distribution and mode of formation, has been divided into categories based on the chemical composition class.

THE CARBONATE MINERALS

There are three polymorphs of calcium carbonate which occur in nature: calcite, aragonite and vaterite in order of decreasing stability. Vaterite is very rare, and unknown in the cavern environment.

The occurrence of aragonite in caves is probably the most puzzling and most investigated cave phenomena. Chemical data predict that aragonite could only be stable at a low cave temperature (say 25°C.) when the pressure is above 3000 atmospheres. Aragonite, however, is amongst the most common cave minerals with world-wide distribution.

Consequently, the mechanism for its formation is believed to be controlled by trace elements, the carbonate-ion itself, supersaturation, and fundamental

mechanisms of nucleation and crystal growth of the pure polymorphs of calcium carbonate, in the cave environment. Aragonite is about 16 per cent more soluble than calcite, and hence unstable with respect to it. However, both are stable with respect to the ions in solution during precipitations when the supersaturation with respect to calcite exceeds the solubility of aragonite. Curl (1962) proposed that under these conditions, the relative rates of crystal nucleation and crystal growth determine which polymorph will dominate.

It has been found that certain trace amounts of impurities and certain conditions of temperature can have a profound effect on whether aragonite or calcite appears. Murray's (1954) experimental studies showed increases in the percentage of aragonite with the increase of magnesium concentration. Wray and Daniels (1957) found that aragonite formation was enhanced under conditions which normally would favour calcite if strontium, barium or lead were present. Also, the excess of carbonate ion promoted increasing amounts of aragonite precipitation. Curl (1962) synthesised these factors by proposing that strontium, magnesium and other metallic ions may induce the precipitation of aragonite or calcite either by 1) providing isomorphous nuclei, 2) modifying relative growth rates, or 3) by causing lattice distortions after adsorption, which will lead to the creation of the crystal lattice dislocations to aid growth. Temperature factors would modify the rates of these mechanisms. Consequently, the problem of the origin of calcite or aragonite in any precipitation can be considered as a competition between nucleation and growth for the two polymorphs. Whichever one can accomplish nucleation sooner and grow more rapidly will dominate.

Calcite is the most common of all the cave minerals, and forms the bulk of all major cave formations. Ultimately, the calcite which forms speleothems comes from the dissolving of the overlying limestone strata. On and near the surface, decaying vegetable matter produces carbon dioxide concentrations, which combine with water in the soil to produce carbonic acid. The acid dissolves minor amounts of limestone as it slowly descends to deeper depths. The acidified soil water dissolves calcium carbonate, until it reaches saturation, all the way down to the cave. Eventually, part of this water will be exposed to the cavern air. The dissipation of the carbon dioxide to the cave air causes a direct precipitation of the calcite.

The effects of geography and climate are very important with respect to the relative abundance of calcite formation. The rate at which carbon dioxide is produced in the soil is proportional to the amount of bacteria and other organisms promoting decay of the vegetable matter. This, of course, is more prevalent in the warmer climates, particularly closer to the equator. Likewise, Arctic caves lack speleothems entirely. Also, stalactites will tend to form in the parts of the cave where carbon dioxide gas will have a better chance of escaping. The better ventilated portions will have the lower carbon dioxide gas accumulations, and more speleothems.

Despite the fact that many of the great karst areas of the world are in dolomitised limestone, the mineral dolomite is extremely rare as a *secondary* cave mineral. Its usual occurrence is as a component of "moonmilk," which consists of extremely fine mineral grains held in a relatively stable suspension and having a milky appearance. The most common species present in moonmilk are the carbonates: calcite, dolomite, huntite, hydromagnesite, magnesite and nesquehonite. It is soft, white and like a watery-clay in consistency, occurring on the walls of many caves. The predominant minerals are calcite and hydromagnesite.

These magnesium carbonates are formed as a result of microorganisms breaking down the cave wall. *Macromonas bipunctata*, as well as actinomycetes and algae are the principal organisms. At least six bacteria species are known to have a part in the reactions.

Metallic elements are easily derived from the sulphides in the overlying limestone. Ground water solutions bring iron, lead, zinc and copper bearing solutions into contact with the carbonate ions of the cave environment. These new carbonates are generally quite rare in the cave environment. There are several recorded deposits, though, of the zinc carbonate, smithsonite (Foster, 1951; Bradbury, 1959; Phillips, 1916; Spencer, 1908). Smithsonite is usually thought of as the weathering product of the zinc sulphide, sphalerite. There is only one known observation (Dietrich, 1960) of smithsonite altering to hydrozincite. A few limited regions of the world have considerable hydrothermal mineralisation in karst regions. Cerrusite, a lead carbonate, often occurs in these deposits on the surface of galena crystals. Only Poorfarm Cave, West Virginia, U.S.A., has appreciable deposits of the iron carbonate, siderite. The copper carbonates, malachite and azurite, commonly occur in the upper oxidised zone of copper deposits, especially where limestone is present. In southwestern United States numerous copper mine shafts have broken into small solutional limestone caves, whose walls were coated with these hydrothermally deposited minerals.

THE SULPHATE MINERALS

The sulphate minerals are present in often large quantities in many cave systems throughout the world. The most common representative of this group is gypsum. This mineral is apparently restricted to the drier cave passages, and is almost never found where speleothems are forming. Sometimes after gypsum formations are deposited, the passages have again become moist, causing the gypsum to dissolve and disappear. In many caves, the sodium sulphate, mirabilite, is commonly associated.

The origin of the sulphate minerals is a speleological problem currently under intense investigation by many researchers. Sulphate minerals, particularly gypsum, are present in many limestone caves throughout the world. In fact, many regions of the world have cavern development in extensive stratified gypsum karst. However, when there is no gypsum in the overlying limestone, the sulphate origin is theorised from a number of sources. In Mammoth Cave, the world's third largest cave system, inwashes from an arid, Pleistocene, soil are proposed by Davies and Chao (1959). Three sulphate minerals: gypsum, barite and more rarely celestite, are commonly related to these cavern fills. Davies believes that it is probable that the cavern passages had large pools of water at the time of the fill deposition. The waters would be rich in barium, strontium and calcium ions. As the sulphate ions in the water grew more concentrated, due to continued influx of fills, the most insoluble form, barium sulphate (barite) would be precipitated. Next would be the strontium sulphate (celestite), and finally the more soluble calcium sulphate (gypsum). Consequently, the gypsum speleothems on the walls would be secondary, having been dissolved from the original gypsum outside the cave entrance, and reformed in the cave. The idea that sulphides elsewhere in the stratigraphic column (Weller, 1927; Pohl and White, 1965) are responsible for sulphate deposition in the cave is very popular, and probably offers the best explanation. Disseminated pyrite is ultimately the major source, but complex inorganic and organic chemical factors have been proposed to weather and transport the ions. With the weathering

of pyrite in a pH condition near neutrality, as it would be if in contact with carbonates, the sulphate ion should be formed. The bacteria *Thiobacillus thiooxidans* and *T. ferrooxidans* are noted (Pohl and White, 1965) in this mechanism to be significant in lowering the pH of the acidic reaction. The iron would remain in the sediment as an insoluble iron oxide and hydroxide. Cavern passages are sparsely distributed generally, and the sulphate bearing solutions would reach passages on all levels in the limestone, not only the uppermost passages.

In dry air at ordinary temperatures, the magnesium sulphate, epsomite, tends to lose water, altering to hexahydrate. This process is particularly notable near the cave entrances. Likewise, mirabilite will rapidly decompose to thenardite.

There are five other known sulphate minerals occurring in the cave environment. Ardealite, $\text{Ca}_2\text{HPO}_4\text{SO}_4\cdot\text{H}_2\text{O}$, from Csoklovina Cave, Rumania and leconite, $\text{NaNH}_4\text{SO}_4\cdot 2\text{H}_2\text{O}$, both represent an early stage in the breakdown of bat guano (Taylor, 1858; Moore, 1970). Pyrite and marcasite, both very common sulphides, are probably the ultimate source for much of the iron and sulphur elements found in the various secondary cave minerals. Wilson Cave, Nevada, U.S.A., has the iron sulphate, melanterite, associated with stalactitic limonite. This limestone cave, in particular, has thick lenses of massive pyrite in the strata above and to the side of the void (Young, 1915). Likewise, this origin would account for the jarosite found in Tintic Cave, Utah (Stringham, 1946). The rare mineral boudantite, $\text{PbFe}_3\text{AsO}_4\text{SO}_4(\text{OH})_6$, is reported from only one cave. It is probably an oxidation product of galena, pyrite and arsenopyrite in the overlying strata, and transported to this Virginian cave by circulating ground waters.

THE SULPHIDE MINERALS

The lead, zinc and iron elements form the only known sulphide mineral species in the cave environment. In certain instances, the concentration of the minerals is great enough, and extensive enough, to promote commercial mining of the cave. The crevice lead-zinc deposits of northwestern Illinois dolomites are a case in point. These deposits were formed by the following genesis: 1) a period(s) of diastrophism that fractured the rock, 2) erosion during which ground water dissolved the carbonate rocks along joints and in brecciated zones, thus development of solutional caves along joints, enlarging caverns and honeycombed rock, 3) influx of hot hydrothermal solutions from depth into the zones of low pressure near the surface, and finally 4) precipitation of the sulphides in the breccia zones, caverns and open joints. The principal sulphides formed are the lead sulphide, galena, and the zinc sulphide, sphalerite (Bradbury, 1959). The iron sulphides, pyrite and marcasite, as well as calcite are often associated.

There is one reported (Kaye, 1959) occurrence in a cave of another sulphide, pyrrhotite. Its identification, however, is uncertain, as it occurs only in trace amounts as small magnetic platy grains in Playa Pajaro Cave on the Isla Mona, Puerto Rico.

VANADATES AND HALIDES

Uranium and vanadium minerals are very rare in the cave environment, though several species are reported from the Tyuya-muyun Cave in Fergana, U.S.S.R. (Chirvinsky, 1925). Cavities in the wall were lined with botryoidal, crystalline masses of calcite, malachite, barite, turanite and other minerals. Masses

of dark-brown compact limestone were cut by coarsely crystalline calcite. Associated with these are lenses of tyuyamunite, $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot n\text{H}_2\text{O}$, which occurs as secondary scattered platy grains. Sometimes the mineral forms compact crypto-crystalline masses. As pointed out, turanite, a copper vanadate, and ferghanite, a uranium vanadate, are believed to be leachate products of the tyuyamunite. Vanadinite is another rare cave species known only in two caves: Havasu Canyon Cave, Arizona, U.S.A., and a cave encountered in the Kopje No. 1 Mine in Broken Hill, Rhodesia (McKee, 1930; Spencer, 1908). In Broken Hill, this mineral is associated with hopeite, hemimorphite and tarbuttite as encrustation on bone breccias.

Fluorite is a common mineral in the Halide Group, and of widespread occurrence. It is, however, only known from two localities. These are Kootenay Florence Cave, British Columbia, Canada, and in Spirit Mountain Cave, Wyoming. Also in this category is halite, whose occurrence in caves is limited to Australia.

THE PHOSPHATE MINERALS

The phosphate minerals are the largest group of cave minerals, but contain some of the rarest species. The ultimate source of the phosphate is the decomposition of bat guano. Fresh bat guano contains about 4 per cent phosphorous

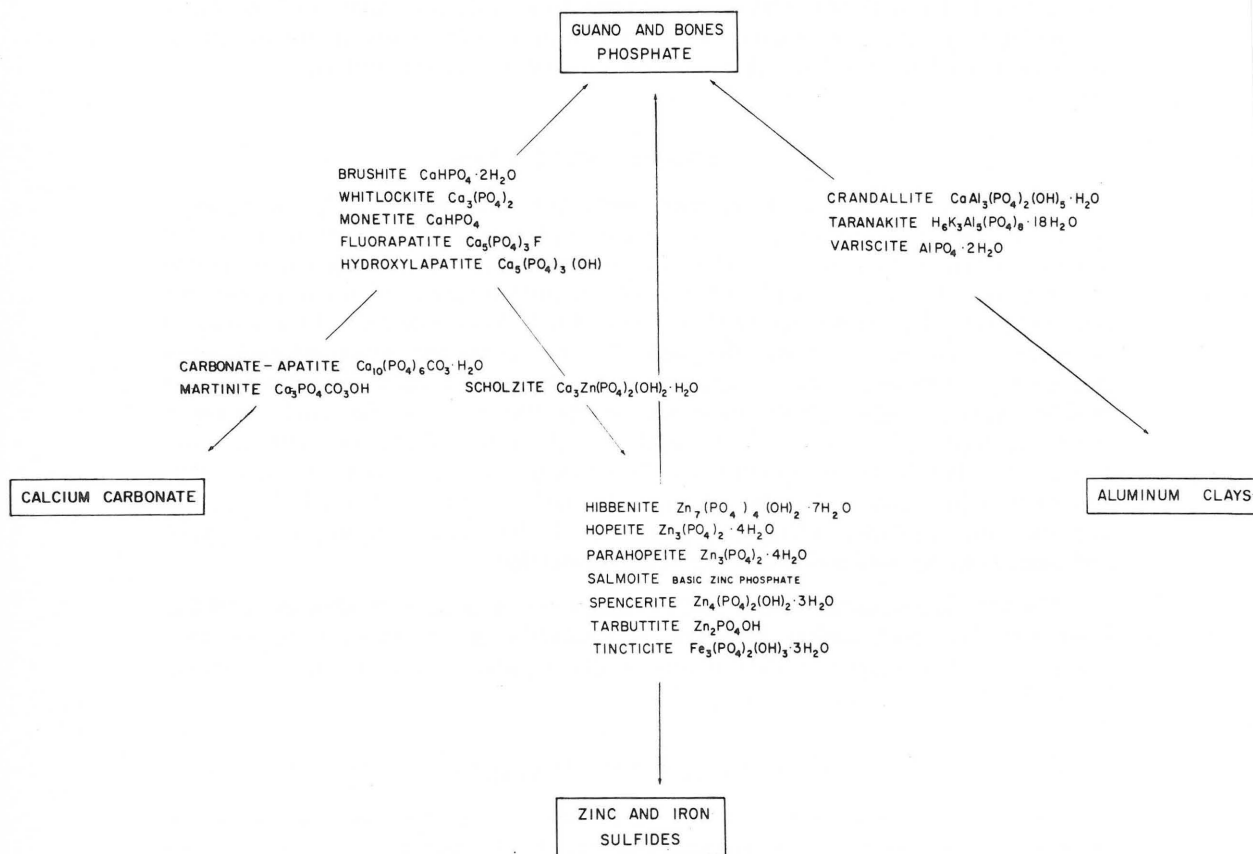


Table 1. Phosphate minerals derived from the reaction of bat guano with wall rock, clay fill, and sulphide mineralised ground water and wall rock.

and 12 per cent nitrogen. Consequently, a series of nitrate and phosphate minerals is possible. The known cave minerals derived from leached guano interactions with the wall rock, with cave fill and with mineralised solutions, are listed in Table 1. The leached bat guano products typically occur as thin crusts and earthy textured aggregates below and adjacent to mounds of dessicated guano. Several of the zinc phosphates are often found as crystals a few millimetres in length, in cavities in decaying bat bones, and lining cracks and cavities in bone matrix deposits. The cave phosphate minerals are still a field of active research in speleology, as most of their stability relationships are still unknown. In fact, it is quite probable that several new species will be found, in the future, in this group of minerals.

OXIDES AND HYDROXIDES

Iron and manganese oxides are very common in caves. Goethite is the typical rusty brown stain found in most caves. Rarely haematite is encountered in the cavern environment, but is metastable as cold ground water could react with it to form the more stable goethite. The manganese minerals, mainly psilomelane and birnessite, often form soot-like layers that cover walls and coat cobbles in cave streams. These deposits are often laminar. Moore and Nicholas (1964) note the important role played by microorganisms in manganese oxide (wad) formation and deposition. The bacteria utilise the organic part of the complex molecules, thus freeing the manganese ions and causing the cave water to become supersaturated with manganese near the bacterial colonies. Birnessite or psilomelane would then be deposited on the rock surface at these sites. Sometimes the manganese oxides will be mixed with oxides of other metals, usually the iron oxides. There is a reported case of copper and manganese oxides mixing in Calumet Cave, Arizona (Ransome, 1904). In this southwestern United States cave the damp walls were coated with black botryoidal growths. Although the black copper oxide crystalline form (tenorite) was not observed, its earthy variety, called melaconite, is probably the mineral species.

Gibbsite is a low temperature hydrothermal mineral normally found in cavities in alkalic and aluminous igneous rocks. It often occurs with boehmite and diaspore in earthy bauxite deposits in paleokarsts. As for specifically occurring in a solutional cave, it has been tentatively identified in a few Pennsylvanian caves by White and Ellisher (1959).

The most common oxide cave mineral is ice. Ice is characteristic of glacier caves, many lava tubes and other "ice caves." It is also found near the entrance of many solutional limestone caves. The coming of freezing winter temperatures often fills the entrance passages with countless frozen ice stalactites, stalagmites and columns. While running water may occasionally be a primary source for ice formation, ordinary seepage is the usual source. Frost crystals on cave walls are undoubtedly the result of condensation of the atmospheric moisture.

THE NITRATE MINERALS

The cave mineral nitrocalcite is the essential component of the so-called saltpetre caves. Through a relatively simple chemical reaction, this calcium nitrate is converted into the potassium nitrate usable for gunpowder. Due to the extreme solubility of potassium nitrate, it is very rarely found naturally in the cave environment. Its existence has been authenticated only in caves of the arid regions of Central Australia (Mawson, 1930). Some caves that have saltpetre deposits show no evidence that they are inhabited by bats. In circumstances like this, the

dried urine of cave rats has been postulated as the nitrate source. Two other nitrate minerals are known from caves. They are nitramite and nitromagnesite.

THE SILICATES AND ALUMINOSILICATES

Secondary quartz is very rare in the cave environment. The presence of euhedral quartz crystals in Wind Cave, South Dakota (White and Deike, 1962) is an indicator of a high temperature solution during formation. At low temperatures (cold ground water) the amorphous form of silica is usually found, and large amounts of opal have been reported in several Black Hills, South Dakota, caves. Hydrothermal water temperatures of 100° to 200° C. are necessary for the growth of quartz crystals, and thus not typical of the cavern environment. Microcrystalline quartz is quite commonly found in the caves, but merely represents eroded fragments of chert nodules that were originally in the limestone strata. A very unusual speleothem exists in Jewel Cave, South Dakota. Deal (1964) reported that these all-silica helictite-stalactite speleothems represent the precipitation of crystalline quartz on the undersides of chert ledges, and reach lengths of 40mm and diameters of 8mm.

The clay minerals in the cave environment are usually deposited as fill washed in from the surface. Consequently, they are not truly representative of secondary mineralisation. This, however, is not always the case, as in many caves, the source of the clays is uncertain, and can sometimes be shown that it is derived from the cavern wall rock. Of these, montmorillonite and illite form the bulk of the cave clay minerals.

Endellite, a species of the kaolinite group, has been reported by Davies and Moore (1957) to be of secondary origin in Carlsbad Caverns, New Mexico. The dehydration product of halloysite, known as metahalloysite, is reported from Cave Mountain Cave, West Virginia (Haas, 1962). A minor clay mineral group, the palygorskite group, is also known from caves. Two of its members, attapulgite and sepiolite, as well as the palygorskite species are recorded in the literature. The attapulgite occurs in well cemented cave fill in Lower Cave of Carlsbad Caverns, U.S.A.; the sepiolite is known from Zbrazov Cave, Czechoslovakia, associated with huntite; the palygorskite in Broken Hill Cave, New Zealand. The zinc silicate, hemimorphite, is known from one cave, that cut into by the Kopje Mine No. 1 on Broken Hill, Rhodesia. The hemimorphite is present with hopeite, tarbuttite and smithsonite as crystallised crusts on the bones and bone-breccia of the cave floor.

MINERALOGY OF STALACTITES

Of the more than 80 mineral species discussed above, almost one-third are known to have stalactite-stalagmite forms. In several instances these 24 minerals may form only a small fraction of the stalactite. They are:

Aragonite	Hydrozincite
Azurite	Ice
Barite	Malachite
Beudantite	Melanterite
Calcite	Mirabilite and an unnamed sodium hemi-
Carbonate-Apatite, var. francolite	calcium sulphate dihydrate in phase
Cerrussite	with the mirabilite
Epsomite	Parahopeite
Goethite/limonite	Scholzite
Gypsum	Smithsonite
Halite	Spencerite
Hemimorphite	Quartz
Hopeite	

CONCLUSION

Speleogenesis is an old, well established study among researchers. The theoretical aspects of cave mineralogy are just beginning as a discipline. No longer are researchers merely limiting their efforts to the classic calcite-aragonite genesis problem. The study of the complex carbonate-organic residue-metal bearing ground water interactions is becoming an active and challenging field. Technical advances in instrumentation such as the scanning electron microscope are being applied with success. Yet, the basic cave mineralogy is still a relatively unknown area. We have not yet fully detailed what mineral associations are present in the cave environment reactions, nor do we fully understand elemental sources for many components. The thermodynamic kinetics of many cave environment mineral reactions, particularly the phosphates, are still unknown. This, and detailed clay mineralogical studies, are promising fields of research for future speleologists and cave-mineral specialists.

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