Chapter I.7

SPELEOTHEMS AND CAVE MINERALS IN GYPSUM CAVES

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Abstract

For many years gypsum karst was considered to contain little of interest from the point of view of chemical deposits. Relatively recently a general study of speleothems has begun within gypsum karst areas in different climatic zones around the world. So far this ongoing research has shown that gypsum karst can be very interesting in terms of its contained chemical deposits. In this chapter, all that is currently known about speleothems in gypsum caves is reported systematically, and the distinctive climatic control over them is emphasised.

1. Introduction

Gypsum karst has long been thought of as a second-class phenomenon, far less interesting than limestone karst from the point of view of the speleothems that it contains. Only since the nineteen-eighties have cavers and scientists realized that gypsum karst may develop unusual epigean and hypogean forms and chemical deposits, which are commonly just as interesting as those in limestone. Speleothems are generally uncommon in gypsum caves and therefore papers discussing the genesis of chemical deposits in these caves are rare. Recently a widespread study has begun on gypsum karsts in different climatic zones around the world. This research is still in progress but has so far shown that gypsum karst can differ significantly from limestone karst with respect to its speleothems, and particularly that several unusual chemical deposits are developed locally within it.

Until now, however, very few studies have been made on chemical deposits (speleothems and secondary mineralization) in the world's gypsum caves, and most of the few detailed studies have concerned Messinian and Triassic gypsum sequences in Emilia Romagna, Italy. Some specific research has recently been undertaken in other parts of the world (including Spain, the United States, the former Soviet Union, Cuba and Argentina), though as yet the distribution of this research coverage is patchy, or it is only partially complete. This chapter reviews all that is known about speleothems (calcite and gypsum), with particular reference to those forms that are found exclusively in the gypsum environment. An updated list of secondary cave minerals is also provided and, finally, the fundamental role exerted by climate in controlling all secondary chemical deposits in gypsum caves is discussed.

2. Speleothems

Speleothems in gypsum caves exist essentially as calcite and gypsum deposits; these two categories are considered separately.
2.1. Calcite speleothems

Calcite speleothems are reasonably widespread in gypsum karst areas, though limited areally by climatic conditions. Their maximum development occurs in areas of temperate continental climate (like Emilia Romagna, Italy), or in pluvial tropical zones (such as in Cuba). Stalactites, flowstone, splash concretions and cave pearls are the most common forms, and they show no morphological peculiarities to distinguish them from similar, but far more common, deposits in limestone caves (Maksimovich, 1969, 1972). It should be noted though, that in most cases their depositional mechanism is unlike that which dominates in the limestone environment (supersaturation caused by diffusion of carbon dioxide into the cave atmosphere). In fact, calcite speleothems have commonly been noted in gypsum successions where there are no superimposed calcareous strata. Thus, the most usual origin of calcite speleothems in the gypsum karst environment cannot be dependent upon re-deposition of calcite that was dissolved earlier by seeping rainwater. Not until the early nineteen-eighties (Forti & Rabbi, 1981) was it demonstrated that calcium carbonate deposition in such cases is controlled by the presence of carbon dioxide dissolved in infiltration water. The formation of calcite speleothems in gypsum caves is no more than a product of the incongruent dissolution of gypsum by water with a high initial carbon dioxide content. A distinctive characteristic of calcite speleothems formed by this mechanism is that they are almost inevitably found a few metres, or a little more, from the point where the water inlet enters the void in the gypsum rock.

Incongruent dissolution explains not only the origin of normal speleothems in many gypsum caves, but also the existence of unique forms (observed only in this environment) comprising crusts detached almost completely from highly corroded gypsum walls. The same mechanism is also responsible for the development of large (14m high, 2m wide and typically less than 20cm thick) "calcite blades" with mud nuclei (see Fig.1) that are present in some Italian and Cuban caves (Forti & Rabbi, 1981; Forti, 1991, 1992).

![Fig. 1. The origin of “bladed flowstones”: A) flowing water dissolves gypsum wall rock and leaves insoluble clay residue behind while simultaneously depositing calcite flowstone over the clay; B) the flowstone protects the underlying clay and mud, thin “bladed flowstone” is produced; C) the process is repeated again, and so forth, until a series of thin blades is left, arranged parallel to the wall (D) (After Hill and Forti, 1986).](image-url)
The strangest calcite speleothem type, which occurs only in the gypsum environment, has been reported from a single cave (the Grave Grubbo, Calabria, Italy), where an unusual type of cave bubble (half bubble) has been found (Forti & Chiesi, 1995). These speleothems develop due to a peculiar form of incongruent dissolution. Carbon dioxide is supplied by the progressive oxidation of suspended organic matter in an underground, sulphide-rich, river. These unique speleothems consist of multiple calcite half-bubbles, from 0.2 to 1.2 cm in diameter, cemented to each other and floating on a pool surface (see Fig. 2). The “half-bubbles” were deposited due to the oxidation of organic matter in an environment that is saturated with gypsum. Oxidation of organic matter in the cave water causes evolution of a long-lasting foam floating on the pool surface and simultaneously supplies a large amount of carbon dioxide. This reacts with Ca\(^{2+}\) ions in the foam’s gypsum water film, forming calcite micro-crystals. These in turn become cemented within the lower part of the bubbles. This process goes on until the bubbles eventually explode, causing “calcite half bubbles” to form.

While considering how rapidly calcite speleothems develop in a gypsum environment, it was observed that, contrary to what might be supposed, the development velocity is commonly higher than that of similar forms in limestone caves. Experimental observations have demonstrated a growth rate of almost 1 mm/year for some flowstones (Dal Monte & Forti, 1995). Faster growth rates of calcite speleothems in gypsum environments relative to those in limestone are clearly associated with the exceptional efficiency of the incongruent dissolution process (Forti, 1991, 1992).
Lastly, it has been noted that there is a difference between what happens in limestone caves and gypsum caves with regard to the formation of structural bands within calcite speleothems. In gypsum caves, rather than speleothems displaying an annual cyclicity, a much higher frequency of banding is typically present (Cazzoli, 1988). The explanation of this is again related to the incongruent dissolutional mechanism, which is active only in the first few metres of percolation inside the gypsum. Close to the surface impulses caused by individual rainfall events are still important, and frequent hiatuses in the water supply potentially lead to the evolution of a new growth layer with each stop and start in the precipitation.

2.2. Gypsum speleothems

Despite the aspects discussed above, it is the gypsum speleothems and crystal forms that hold the strongest elements of interest, as well as having a more ubiquitous distribution. Gypsum speleothems present obvious morphological differences compared to calcite ones, due to their distinct genetic mechanism, which involves supersaturation due to evaporation. Gypsum stalactites are typically more contorted, spotted and multi-branched. In most cases their growth depends much more, if not exclusively, upon surficial percolation water rather than upon water that feeds through a central tube. This commonly results in the central tube being absent, or partially (if not completely) obstructed.

The effect of permanent air currents (or at least those that are active during the stalactites growth periods) is the exact opposite with respect to calcite and gypsum stalactites. In fact, in the case of the former, as the growth mechanism is controlled by carbon dioxide diffusion, which is not influenced in any way by the air current, there is commonly a deviation of the stalactite in the direction of air movement, which is the same direction that the water droplets are deviated before they fall. In the case of gypsum stalactites, the inverse effect dominates, as the speleothems deviate towards the source of the air current, where maximum evaporation occurs.

In the hot and dry zones of New Mexico a still more complex evolution of deflected gypsum stalactites is observed. This phenomenon takes the form of stalactites shaped like an “elephant’s foot”, presenting a notable swelling that is commonly inclined downwards close to the top (Calaforra & Forti, 1994; Chiesi & Forti, 1996). These gypsum stalactites owe their genesis to a combination of factors that are rarely found together at a single locality. In fact, these speleothems form only when they are situated in a constant air current, and are fed by slightly undersaturated water (condensation water). Moreover, the temperature must be high enough to guarantee rapid evaporation, thus allowing saturation to be achieved at a well-marked level on the speleothem (the site of the swelling).

Stalactites are found quite commonly in Italian caves, but stalagmites are relatively rare. This “rarity” is basically a reflection of the climatic conditions, which allow the easier evolution of inflorescence so that capillary uplift and evaporation can take place. In areas of warmer, dryer climate (such as Sorbas, in Spain, and New Mexico) stalagmites are as common as stalactites (Calaforra et al, 1992).

The fact that evaporation, is the dominant genetic mechanism during the evolution of the
Evaporation and gypsum deposition

Capillary movement of the seeping water towards the wall surface where evaporation occurs.

Fig. 3. Evolution sketch for the gypsum balls in the karst of Sorbas (Spain): A) the horizontal disposition of the gypsum strata with thin clay interbeds drives the capillary movements of the seeping water to the wall surface where evaporation occurs; B) the cross-section of the gypsum ball shows its spherical growth and the rotation of the c axis of the gypsum fibres to become perpendicular to the rising surface; C) cross-section parallel to the bedding plane showing the development of gypsum balls just in the places intersected by preferential capillary flows (After Calaforra and Forti, 1993).

gypsum deposits, explains why some types of speleothem, common in calcite, are very rare in gypsum, and vice versa. Compared to calcium carbonate, gypsum forms helictites with extreme difficulty. This is because, as already mentioned, evaporation leads to an even greater obstruction of the feeding capillaries than is normally characteristic of these speleothems in calcite. Small gypsum helictites have been found only in a single cave in Sicily (Italy), (Forti, 1987). In contrast, it is much easier for wind-related speleothems, such as rims and trays, to develop in this environment (Chiesi & Forti, 1992; Calaforra & Forti, 1994).

Gypsum caves also host unusual speleothems, like “gypsum balls” and “hollow stalagmites”, both described from the Sorbas caves (Spain) (Calaforra & Forti, 1993; Calaforra, 1996). The balls (see Fig.3) are layered, spheroidal gypsum formations (up to 10cm in diameter) with an internal structure consisting of radially elongated crystals. They develop on the cave walls along sub-horizontal layers with thin limey, sandy interbeds, and are found exclusively in the deepest parts of the caves, where water flow and supersaturation remain constant. The sub-horizontal disposition of gypsum layers with thin clayey interbeds favours capillary drainage of supersaturated water towards preferred places in the cave walls, where evaporation and precipitation can proceed, allowing the evolution of the gypsum balls. Normally, the gypsum balls are compact and consist of lengthened gypsum fibres that assume a radial structure. As they mature, such speleothems may evolve an internal drainage tube inside a related clayey interbed. The consequent arrival of water, sometimes unsaturated, at the level of the balls can, in some cases, cause the emptying of the balls, and sometimes their complete destruction.

Hollow gypsum stalagmites (see Fig. 4) have been reported from a cave in the Sorbas area...
Fig. 4. Steps in the evolution of gypsum hole stalagmites: A) development of a normal stalagmite due to oversaturated dripping during a semi-dry period; B) undersaturated leakage forms a hole in the stalagmite during a wet period; C) capillary uplift and evaporation in dry periods, showing the evolution of the first conical segment of the stalagmite; D) a new wet period refills the stalagmite with water and the subsequent dry period (E) causes the development of another conical segment; F) final shape of the hollow stalagmites (After Calaforra and Forti, 1993).

(Spain) and from a cave of New Mexico (Calaforra & Forti, 1993). They are very narrow and up to 150 cm tall stalagmites, with an external diameter of no more of 4-6 cm and an internal tube that is 2-3 cm in diameter and commonly reaches the bottom of the stalagmite. In both known occurrences these speleothems were observed close to the land surface, where fresh seepage water can arrive very rapidly. The climate of both areas (hot and dry, with rare rainstorms) is fundamental to the development of hollow gypsum stalagmites. During short, intense wet periods, infiltration water reaches the cave passages undersaturated with respect to gypsum and is capable of "drilling", or at least keeping open, the central tube in the stalagmites. In dry periods (practically all of the year), capillary-evaporation processes related to the water stored inside the tubes of the stalagmites causes the growth of their tops.

Gypsum crystals, between several microns and more than a metre in length, are without doubt the most common secondary deposit found in caves at all latitudes and in all climatic zones. They are commonly found as free deposits, though more typically they form druses anchored to the cave walls. The smallest gypsum crystals (from 10-100 microns) are found widely in the form of "gypsum powder" deposits, which can develop due to several different mechanisms. They may cover the ice flows in Siberian caves (Forti, 1990, 1991), deposited due to fractional crystallization during freezing. In the gypsum caves of New Mexico, they can cover the cave walls during brief periods in between rainstorms (Calaforra & Forti, 1994). In this situation the gypsum powder develops due to sudden evaporation of capillary water that reaches the cave walls just after a flood. Gypsum powder also forms over large deposits of guano in areas of temperate climate, and in such cases the deposits develop by the mineralization of guano in a strongly sulphate rich environment (Forti, 1989). Finally, gypsum powder can be a rehydration product of bassanite in tropi-
SPELEOTHEMS AND CAVE MINERALS IN GYPSUM CAVES

Fig. 5- Evolution of gypsum flowers over calcite speleothems in the gypsum caves of Bologna: water oversaturated with respect to calcite flowing over the wall and the floor of the caves deposit calcite flowstones. A part of the same water is driven by capillarity on top of the speleothem's roughness where it evaporates giving rise to gypsum flowers.

Gypsum flowers, which represent the genetic analogues of calcite coralloids, are practically ubiquitous, and owe their genesis to evaporation of a thin water film that is drawn slowly up wall discontinuities, driven by capillarity. Their evolution is relatively rapid and appears identical to that of the calcite or aragonite coralloids in limestone caves. The unique feature displayed by these gypsum outgrowths is that of being highly sensitive to air currents. In gypsum caves it is common to see such formations with gypsum macro-crystals elongated toward the wind direction. A classical case is provided by the wind controlled flowers that develop inside "gyypsum chimneys", which are sub-vertical corrosion-condensation conduits that develop where there is a continuous strong, hot and humid air current flowing upwards, in the karst area of Neuquen in Argentina (Forti et al., 1993).

Another relatively unusual type of inflorescence, though more common in caves with a humid temperate or tropical climate, takes the form of the gypsum crystals growing over active calcite speleothems (Fig. 5). This occurs notwithstanding the fact that the gypsum precipitation mechani-
sm is completely different to that of calcite in a gypsum cave. The calcite precipitates due to diffusion of carbon dioxide into the cave atmosphere, or following incongruent dissolution, whereas the gypsum is deposited as a result of supersaturation due to evaporation. (Forti & Marsigli, 1978)

3. Cave minerals

When considering the other secondary minerals that can be found inside gypsum caves, it must be remembered that up until the early nineteen-seventies only two minerals had been identified (Laghi, 1806; Bertolani & Rossi, 1972). This situation arose primarily because practically nobody was interested in this specific area of study. Also, there was a well-rooted opinion that if the world’s gypsum caves were poor in concretions, they would also be completely devoid of secondary minerals. Specialized research in this field has only begun during the last 15-20 years, but even then only in a few areas. First among these is the Emilia Romagna region, followed by others in Italy, the United States and Argentina, Ukraine (Forti, 1986a,b; 1989; Turchinov 1993). Though the extent of this study is evidently limited it has shown that effectively the gypsum cave environment is not rich in minerals. This is logical, if it is realised that gypsum rock is a salt of a strong acid (sulphuric acid) and therefore shows much less tendency than does limestone to react with any mineralizing agents that are potentially present in the cave environment.

Notwithstanding the limited research activity, occurrences of more than 20 minerals with distinct characteristics (summarised in the table) have already been described (Cervellati et al, 1975; Forti & Querzë, 1978; Rogozhnikov 1984; Chiesi & Forti, 1985, 1986, 1988; Forti, 1993; Turchinov 1993; Carrozzini et al, 1996; Turchinov 1996). It is likely that new varieties of mineralization will be located in the near future. It must be noted here that about half of the minerals

![Fig.6- Sketch for the simultaneous dissolution of gypsum and deposition of skeletal quartz in the Monte Mauro caves (Italy): the anaerobic reduction of sulphates to sulphides with the oxidation of organic matter to CO2 lowers the pH, making possible the precipitation of silica and induces a slight undersaturation with respect to gypsum which is therefore dissolved (after Forti 1994)](image)
already recorded have been found in caves where sulphide water is present or where processes connected to the sulphur redox cycle are active (Forti & Rossi, 1987, 1989; Forti, 1994).

A particularly important find was made in the cave of Vena del Gesso Romagnola (see Fig.6), where euhedral quartz crystals had developed upon corroded gypsum crystals, at normal temperature (Forti 1993, 1994). This find is highly significant, not only in the context of the karst environment in general, but also because it demonstrates how quartz can form naturally, even at low temperatures. These conditions are very different to the low to medium temperature conditions previously considered necessary for quartz crystal formation. The mechanism that brings about quartz deposition and concomitant gypsum corrosion is connected to the reduction of sulphates to sulphides in a phreatic environment, and it may be one of the most important mechanisms involved in the embryonic stages of karst cavity origin in gypsum.

4. Climatic influence on the chemical deposits

Climatic factors have a strong influence upon what type of chemical deposit can be found in a gypsum cave (Calaforra et al, 1992; Calaforra, 1996). In general speleothems are less abundant in cavities in gypsum than they are in limestone caves, though some exceptions do exist. As described above, two broad types of chemical deposit can be seen in gypsum caves, these being gypsum speleothems and calcium carbonate (normally calcite) speleothems. Some caves present both deposit types simultaneously, while other caves present just one or the other. The depositional mechanisms of the two minerals are totally different in the karst environment: gypsum can only be deposited through supersaturation due to evaporation, while calcite is deposited in response to the release of carbon dioxide into the cave atmosphere or as one effect of incongruent dissolution.

These mechanisms are influenced in different ways by climatic variables, and therefore the local climate dictates the kind of chemical deposit that may develop in any given cave. There are no speleothems at all (either calcite or gypsum) in the polar regions, because extremely low temperatures prevent evaporation and, hence, deposition of gypsum. Moreover, during periods of thaw the rapid flow of water with minimal mineral content does not encourage the growth of calcite speleothems. The only chemical deposit so far observed under these conditions is a distinctive form of gypsum powder, which accumulates over ice flows during the winter periods (Forti, 1990).

Calcite speleothems in gypsum caves are found mostly in temperate humid areas, where the hyperkarst mechanism of gypsum corrosion (Forti & Rabbi, 1980) is particularly active. Gypsum speleothems are also normally present in these regions, especially, in those parts of caves (basal of pits, narrow “squeeze” passages, etc.) where stronger air currents facilitate evaporation and consequent gypsum supersaturation. As the climate becomes less mild, calcite deposits tend to become predominant, until they are the only ones present. This is obviously due to a progressive diminution of the possibility of evaporation.

In areas of hot, arid climate, such as Sorbas (Spain), New Mexico and Arizona, gypsum speleothems are widespread and may grow to a large size, while carbonate formations are effectively
absent. The absence of calcite speleothems reflects the fact that the arid climate prevents development of vegetation cover over the gypsum, minimising the possibility of high carbon dioxide contents in infiltration water, and therefore hindering the process of hyperkarst corrosion of gypsum. The only possible exceptions are deep drainage tubes where transported organic materials (essentially vegetation) can accumulate during flooding episodes. This material oxidizes during dry periods, supplying the environment with the carbon dioxide that is necessary for the development of carbonate crusts on conduit floors.

In the tropical environment there is a general balance between the presence of carbonate and gypsum concretions. This reflects both the great quantity of vegetation that covers most of the surface, and the extremely hot climate.

It is worth noting that calcite speleothems in gypsum caves can provide excellent palaeoclimatic indicators. In fact, in some Siberian gypsum caves, the mere presence of such calcite speleothems, now in an advanced state of degradation, indicates clearly that the host cavity existed before the last glacial maximum, in a period of more favourable climate, characterized by constant water flows throughout the year. Similar indications have been found in the Sorbas caves in Spain, where residual calcite flowstone that covers pavements inside the larger caves testifies of a humid climate, very different to today’s conditions.

5. Conclusions

Reports of detailed studies of chemical deposits in gypsum caves are still relatively rare, and only a few small parts of the principal gypsum karst areas have been examined systematically from this point of view. Nevertheless, on the basis of the knowledge so far gained, it is now possible to point out some distinct characteristics of these deposits, that differentiate them from their analogues in limestone environments.

What is superficially striking is the relatively small size and the limited variety (especially in terms of mineralogical, but also their morphological, variability) of most of these deposits. This may be one reason for the delay in launching systematic studies. Such studies were considered, at best, of minimal interest, if not of no scientific value at all, until only a few years ago.

Putting this aside, the few systematic studies have all demonstrated how gypsum karst possesses its own unique peculiarities of morphology (particularly in the case of its speleothems) and of mineralogy (in the case of the cave minerals). Therefore, it seems certain that in the near future, with continuing study of chemical deposits in gypsum caves, there will be a large increase in the number of recorded occurrences and known types.

One final aspect of extreme interest should be re-emphasised, and that is how climatic influences dominate almost absolutely during the development of chemical deposits in gypsiferous environments. The role of climatic factors is certainly far more dominant in the gypsum situation than has been verified in limestone caves in comparable climatic situations. This close relationship with climate gives deposits preserved in the gypsum environment a potentially very great importance on the basis of their potential application to palaeoclimatic studies, not just in terms of the interest held by the cave minerals themselves.
<table>
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<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Characteristics</th>
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<tbody>
<tr>
<td>1 - Aluminium oxides</td>
<td>Al₂O₃</td>
<td>Polymineral flowstones with opal, sulphur and iron oxide</td>
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<tr>
<td>2 - Bassanite</td>
<td>CaSO₄.2H₂O</td>
<td>White powdery deposits on gypsum</td>
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<tr>
<td>3 - Brochantite</td>
<td>Cu₄(OH)₆SO₄</td>
<td>Emerald green crusts associated with devilline and penninite</td>
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<tr>
<td>4 - Brushite</td>
<td>CaHPO₄.2H₂O</td>
<td>Yellow pulverescent deposits on guano</td>
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<tr>
<td>5 - Calcite</td>
<td>CaCO₃</td>
<td>Various speleothems</td>
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<tr>
<td>6 - Carbonatoapatite</td>
<td>Ca₅(PO₄,CO₃)₃(OH)</td>
<td>Yellowish crusts on calcitic concretions in contact with guano</td>
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<td>7 - Celestite</td>
<td>SrSO₄</td>
<td>Small crystals over a crust of iron and manganese oxides/hydroxides</td>
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<tr>
<td>8 - Chloromagnesite</td>
<td>MgCl₂</td>
<td>Dispersed within fibres of epsomite</td>
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<tr>
<td>9 - Devilline</td>
<td>Cu₄Ca(SO₄)₂(OH)₆.3H₂O</td>
<td>Emerald green crusts associated with brochantite and penninite</td>
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<td>Acicular crystals on mud</td>
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<td>11 - Iron oxides/hydroxides</td>
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<td>12 - Fluoroapatite</td>
<td>Ca₅(PO₄, CO₃)₃F</td>
<td>Golden crusts with carbonato-apatite on fossil remains</td>
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<td>13 - Gypsum</td>
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<td>14 - Goethite</td>
<td>FeO(OH)</td>
<td>Large crusts, stalactites and stalagmites with limonite and Fe and Mn oxides</td>
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<td>15 - Ice</td>
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<td>16 - Lepidocrocite</td>
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<td>18 - Manganese oxides</td>
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<td>21 - Penninite</td>
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<td>23 - Rhodochrosite</td>
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<td>25 - Sylvite</td>
<td>KCl</td>
<td>Stalactites</td>
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