PROGRESSIVE LOWERING OF THE WATER TABLE IN THE GRAND CANYON, ARIZONA, USA AS RECORDED BY CAVE AND MINE DEPOSITS

CAROL A. HILL and VICTOR J. POLYAK
Earth and Planetary Sciences, University of New Mexico, 200 Yale Blvd. Albuquerque, NM 87131, carolannhill@aol.com

ABSTRACT
Speleothem and ore deposits in Grand Canyon (GC) caves and mines record the progressive lowering of the water table over time. The sequence of significant deposits and events in the GC is: (1) Ore mineralization (Cu-U) episode. Sulfide ore mineralization, as exposed in the breccia pipes/mines of the GC, formed in the reduced zone, possibly during the Laramide when H_2S migrated up deep basement faults and monoclinal structures. Uranium precipitated in the redox zone and calcite spar formed paragenetically with ore mineralization. Time: Paleocene to Eocene? (2) Hematite/goethite episode. The oldest cave deposits are manganese and iron oxides (hematite/goethite) containing minor halite and trace-metals (e.g., As, Ba, Pb). These deposits fill small solution cavities in the Redwall Limestone exposed by cave passages. These metal-rich deposits formed when ascending warm saline waters mixed with descending oxidized cold waters in the deep phreatic zone. Time: Oligocene? (3) Calcite spar episode. Calcite spar crystals are found lining the walls of a number of GC caves. Since they line cave passages, they must be younger than these passages. Large calcite spar crystals are known to form from low-temperature hydrothermal solutions under quiet phreatic conditions. Time: Miocene? (4) Mammillary-replacement gypsum episode. Mammillaries, consisting of microcrystalline fibrous calcite, are a speleothem type that forms in the shallow-phreatic zone just below the water table. Replacement gypsum rinds form at or just above the water table where degassing H_2S reacts with wet limestone. These two cave deposits can be used to determine past water table positions in the Redwall Limestone as well as incision rates for the GC. Time: Middle Miocene-Pliocene in the western GC to Pliocene-Pleistocene in the eastern GC to the present in Marble Canyon. (5) Subaerial speleothem episode. Speleothems such as stalactites and stalagmites record when GC caves became air-filled. Many of these speleothems are very old, surpassing the limit of U-series dating. Time: Pliocene-Recent. U-Pb and U-series dating of mine calcite, calcite-spar cave linings, water-table mammillary calcite, and subaerial speleothem calcite should provide an absolute time scale for the history of water table lowering in, and incision of, the Grand Canyon.

INTRODUCTION

The purpose of this study is to understand the evolution of the Grand Canyon with regard to the progressive lowering of the water table over time, and with regard to the age of incision of the canyon itself. In order to accomplish this goal a number of caves and mines within the Grand Canyon area were visited (Fig. 1). Caves (artesian type only) visited during the course of this study were: Cave of the Domes, Babylon, Crystal Forest, Tse'an Bida, Tse'an Kaetan, Bat, Moria, Mother, Diamond, Grand Canyon Caverns, Cathedral, Indian, Cave Spring, Dusty, Falls, IMAX, Chuar Butte, Muav, and Rampart. Mines visited were: Orphan, Grandview, Grand Gulch, Savanic, Ridenour, Riverview, Pigeon, Snyder, Hack Canyon, Ryan, Petosky, Mackin, Anita (Emerald), Copper Queen, Northstar, and Eaststar.

Two main types of caves exist in the Grand Canyon area: (1) unconfined (vadose) caves, and (2) confined (artesian, phreatic) caves (Huntoon, 2000a,b). Unconfined caves in the Grand Canyon are simple linear drains in the vadose zone where water recharges at the surface of the Kaibab Plateau and moves under high gradients down along faults (or master joints parallel to faults) to the Redwall-Muav aquifer, and where discharge is mainly from the base of the Muav Limestone to the Colorado River. This modern vadose circulation system has given rise to the great North Rim caves such as Roaring Springs and Thunder River. However, no vadose caves were visited during this study because they do not contain deposits within them that record the geologic history of the Grand Canyon. They are caves that discharge *to* the modern Grand Canyon and thus *postdate* the incision of the canyon.

Confined caves in the Grand Canyon come in two varieties: modern and relict. Both of these constitute what is known as the "Redwall artesian aquifer." Modern confined caves are hydrologically active caves that give rise to springs along the Marble Canyon section of the Grand Canyon. They are maze caves that are saturated and inaccessible. Relict confined caves formed like modern confined caves (i.e., under artesian conditions in the phreatic zone), but they have been dissected and dewatered by canyon erosion from west to east over time. Relict Redwall artesian caves are extremely important to understanding the geologic history of the Grand Canyon because they contain remnant deposits that record events that occurred both *before* and *during* the incision of the canyon. These cave deposits are (from oldest to youngest): (1) hematite/goethite, (2) calcite spar, (3) mammillaries-replacement gypsum, and (4) subaerial speleothems (Hill et al., 2001). A specific cave may have only one of these deposits, two or three of these deposits (Fig. 2), or all four of these deposits, but in all cases the relative sequence of these deposits is *consistently* the same.

COPPER-URANIUM ORE MINERALIZATION EPISODE

Some of the highest-grade uranium ore in North America resides in the breccia pipes of the Grand Canyon (Mathisen, 1987). These pipes were mined in the late 1800s-early 1900s for copper and in the 1950s-1960s for uranium. The breccia pipes have their bases in the Redwall Limestone and they stope up into the Paleozoic section and even into the Mesozoic section where these rocks have not been removed by erosion. The ore deposits of the Grand Canyon not only contain copper and uranium, but also a number of different sulfide minerals and pyrobitumen. Wenrich and Sutphin (1989) suggested a paragenetic sequence for these different ore minerals. The rare-metal sulfides (Ni, Co, As) + pyrite-marcasite formed early in the zone of reduction, and then somewhat later the sulfides of copper, lead and zinc also formed in the zone of reduction. Even later the ore-mineral uraninite probably formed in the redox (reduction-oxidation) zone, typical of "roll-front" type uranium deposits, and still later minerals were deposited in the zone of oxidation. Thus, this paragenetic sequence of minerals records the progressive lowering of the water table over time through the breccia pipes.

The general model proposed by this study for the breccia-pipe ore deposits of the Grand Canyon involves two-fluids, where a shallow meteoric oxidizing fluid carrying copper and uranium (as carbonate complexes) from a recharge area to the south mixed with a deep-sourced saline and reducing fluid containing dissolved H_2S, CO_2, and metals (Fig. 3). In this model, the proposed source of uranium and copper is stratabound uranium-copper deposits once present in above-lying Mesozoic rock (still located in the area east of the Grand Canyon), and the proposed source of reductant is hydrocarbons in the Precambrian Supergroup basement. Time of mineralization is debatable. Ludwig and Simmons (1992) performed U-Pb dates on uraninite from a number of mines and found that these ages congregate in the Triassic – although a number have greater or lesser age values. On the other hand, Beitler et al. (2003) placed the timing of migration of H_2S up along monoclines in Southern Utah in the Laramide (Paleocene-Eocene), where this reductant bleached the Navajo Sandstone along monoclinal and anticlinal structures. Therefore it is also possible that Laramide monoclines in the Grand Canyon area were avenues for reductant (H_2S) ascending from Precambrian basement faults into breccia pipes.

HEMATITE/GOETHITE EPISODE

The first event recorded in Grand Canyon caves is the hematite/goethite episode. These deposits occur in cavities within the Redwall Limestone, exposed by later cave passage dissolution. Sometimes these deposits are composed of the higher-temperature iron-rich mineral hematite, and sometimes by lower-temperature goethite. Usually this material is high in manganese, and also in the trace elements of As, Ba, Co, Cu, Mo, Ni, Pb, and Zn. Some deposits contain halite.

The mechanism for the precipitation of hematite/goethite is shown in Figure 4. Thermal waters rising from depth are often saturated with CO_2. Water mixed with gas (H_2S, CO_2) has a slightly lower density than normal water, so it rises along joints and cools. This cooling caused the dissolution of the Redwall Limestone by the "cooling corrosion" mechanism of Bögli (1980). In addition, the mixture of low TDS, low CO_2, shallow meteoric waters with high TDS, high CO_2, deep-seated waters creates a solution that dissolves limestone in the mixing zone. This process is called "mixing corrosion" (Ford and Williams, 1989). Dissolution of carbonate (limestone) consumes H^+ and thus raises the pH allowing for the precipitation of hematite/goethite within the cavities created by the mixing-corrosion mechanism. In turn, the precipitation of hematite/goethite under oxidizing conditions generates acidity according to the following reaction:

$$2Fe^{2+} + 0.5O_2 + 2H_2O = Fe_2O_3 + 4H^+ \qquad (1)$$

The acidity produced in this reaction further dissolves cavities in the limestone. Therefore, the creation of space for the hematite/goethite and the chemistry of its precipitation goes on simultaneously. Time of this episode is uncertain, but it may date from the Oligocene or Early Miocene.

CALCITE SPAR EPISODE

After the precipitation of hematite/goethite the water table continued to descend until the Redwall Limestone was within the maximum solubility regime of calcite (Fig. 5). As convective water rises and cools, the solubility of calcite gradually increases so that cave passages dissolve in the deep "solutional zone." This usually occurs somewhere between ~250-550 m below the water table (Dublyansky, 1995, 2000). It was in this regime that the artesian-phreatic cave passages formed.

As the water table descended further, Grand Canyon caves formed in the "solutional zone" were shifted into the "depositional zone" where the solubility of calcite dropped sharply and solutions changed from aggressive to precipitative (Fig. 5). Since the loss of CO_2 is very slow in the phreatic regime, spar crystals had a chance to grow slowly and large, lining previously formed cave passages (Fig. 6). Spar crystals up to 56 cm long have been found lining Grand Canyon caves. These crystals exhibit carbon-oxygen isotope values, fluid inclusion temperatures, and fluorescence (orange to non-fluorescent) that indicate a low-temperature hydrothermal regime, probably somewhere between ~90ºC to 30ºC.

MAMMILLARY-REPLACEMENT GYPSUM EPISODE

Mammillary linings. As the water table dropped to the level of the Redwall Limestone, the deposition of calcite changed from large spar crystal linings to microcrystalline fibrous "mammillary" linings (Fig. 7). Mammillaries are a type of speleothem that forms within a 100 m or so of the water table, most usually within ~50 m to 0 m (Hill and Forti, 1997). In the shallow phreatic zone near the water table the loss of CO_2 is much faster than in the deep phreatic zone (Fig. 5); therefore, a rapid precipitation of fine-grained fibrous calcite occurs in this regime. The size of crystals in mammillaries typically varies from several millimeters to a few centimeters. Mammillary coatings are very common in Grand Canyon caves, and some coatings line entire caves or cave passages (e.g., Mother Cave).

Mammillary speleothems are important to the study of the Grand Canyon because they denote the approximate position of the paleo-water table and can thus be used to date canyon incision from one end of the canyon to the other. Three separate pieces of evidence support a near water-table origin for mammillaries: (1) the fine-grained nature of mammillaries, (2) the common association of mammillaries with calcite rafts and folia – two speleothem types believed to form at the water table (Hill and Forti, 1997), and (3) the occurrence of mammillaries forming today near the water table along with folia (e.g., in Devils Hole, Nevada; Kolesar and Riggs, 2004). Far below the water table mammillaries cannot form, and above the water table the growth of mammillaries ceases (Fig. 8).

Preliminary dating of mammillaries in Grand Canyon caves indicates that their age is beyond the U-series method (>0.5 Ma). In most instances, the uranium concentration is high enough, and the lead concentration is low enough, for the U-Pb method to be suitable for dating these water-table/canyon incision speleothem indicators. Preliminary results for a mammillary sample from Grand Canyon Caverns on the western end of the Grand Canyon indicate that the water table was at the Redwall level there sometime during the Middle Miocene (~19 Ma) (Polyak et al., 2004). This timing is consistent with the incision record from the dating of basalt flows on the western side of the Grand Canyon by Young (2004). Preliminary dating results from a Bida Cave mammillary sample on the eastern end of the Grand Canyon indicate that the water table was at the level of the Redwall in this part of the canyon sometime during the Pliocene (~2-3 Ma).

Replacement Gypsum. While mammillary speleothems form near or just below the water table, replacement gypsum rinds form just above the water table where H_2S reacts with wet limestone to form gypsum according to the following equations:

$$\underset{}{H_2S + 2O_2} \leftrightarrow \underbrace{H^+ + HSO_4^-}_{\text{sulfuric acid}} \leftrightarrow 2H^+ + SO_4^{2-} \qquad (2)$$

$$\underbrace{2H^+ + SO_4^{2-}}_{\text{sulfuric acid}} + \underbrace{CaCO_3}_{\text{limestone}} \leftrightarrow \underbrace{Ca^{2+} + SO_4^{2-}}_{\text{gypsum}} + H_2O + CO_2 \qquad (3)$$

In the case of Grand Canyon caves, this episode was minor in contrast to the sulfuric acid origin of caves in the Guadalupe Mountains of New Mexico (e.g., Carlsbad Cavern and Lechuguilla Cave; Hill, 1990). This episode probably formed in response to Basin and Range-age tectonic extension, where H_2S from the Precambrian basement ascended to the level of the Redwall Limestone along master joints parallel to faults. Proof that the gypsum rinds in Grand Canyon caves is of replacement, rather than speleothemic, origin is their enrichment in the light isotope of sulfur ($\delta^{34}S$ = -17.9‰ to +5.8‰, avg. -3.7‰ for 9 values), whereas Permian gypsum in the overburden averages about +14-15‰).

In some caves replacement gypsum can be seen directly overlying mammillary speleothems (e.g., Cave of the Domes, Mother Cave). In these cases this sequence of deposits records the lowering of the water table through the cave itself. The mammillary coating formed just below the water table, while later in time as the water table dropped through the extent of the cave, the gypsum rind formed just above the water table in the subaerial zone from the replacement of limestone (eq. 3).

SUBAERIAL SPELEOTHEM EPISODE

After Grand Canyon caves became air-filled, they became decorated with subaerial speleothems such as stalactites, stalagmites, and flowstone. U-series dating has shown that many of the speleothems collected in Grand Canyon caves are very old – that is, beyond the U-series dating method. Today the caves of the Grand Canyon are dry and very few speleothems are still actively growing. Periods of substantial growth of speleothems likely represent climatic episodes of increased precipitation. For example, a stalactite collected from Bat Cave was deposited sometime between 402 and 448 ka, and likely coincides with Oxygen Isotope Stage 12, a global glacial period that could have included increased precipitation for the Grand Canyon area (Shackleton and Opdyke, 1973).

CONCLUSION

The overall model for the progressive lowering of the water table in the Grand Canyon is shown in Figure 9. Essentially, when the water table was high in Mesozoic strata (position (1) in Fig. 9), the Redwall Limestone was in the reduced zone, and this allowed for the precipitation of sulfide minerals in the breccia pipes of the Grand Canyon. The uranium mineralization followed as the Redwall Limestone entered the redox zone. Even later in time in the deep phreatic zone, mixing corrosion caused the dissolution of cavities in the Redwall Limestone and the precipitation of hematite/goethite within these cavities (position (2) in Fig. 9). In the shallower phreatic zone the limestone was first in the "solutional zone" where cave passages dissolved, followed by a shift into the "depositional zone" where calcite spar lined these cave passages (position (3) in Fig. 9). When the water table reached the level of the Redwall Limestone (position (4) in Fig. 9) the mammillaries and replacement gypsum formed, and when it descended below the level of the caves (position (5) in Fig. 9) subaerial speleothems grew within these caves.

Future U-Pb and U-series dating of mine calcite, calcite-spar linings, mammillary calcite, and subaerial speleothem calcite should provide an absolute time scale for the history of water table lowering in, and incision of, the Grand Canyon.

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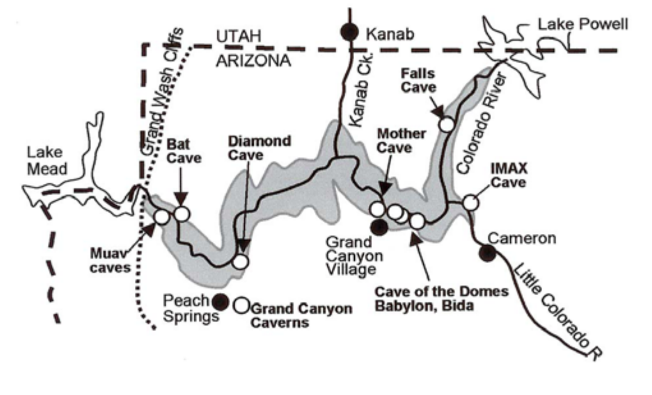

Figure 1. Map of the Grand Canyon and location of the major caves visited during this study.

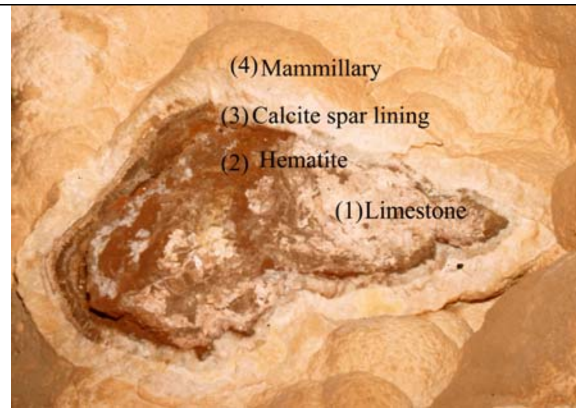

Figure 2. Three of the four types of cave deposits are displayed on wall of Bida Cave. Photo by Bob Buecher.

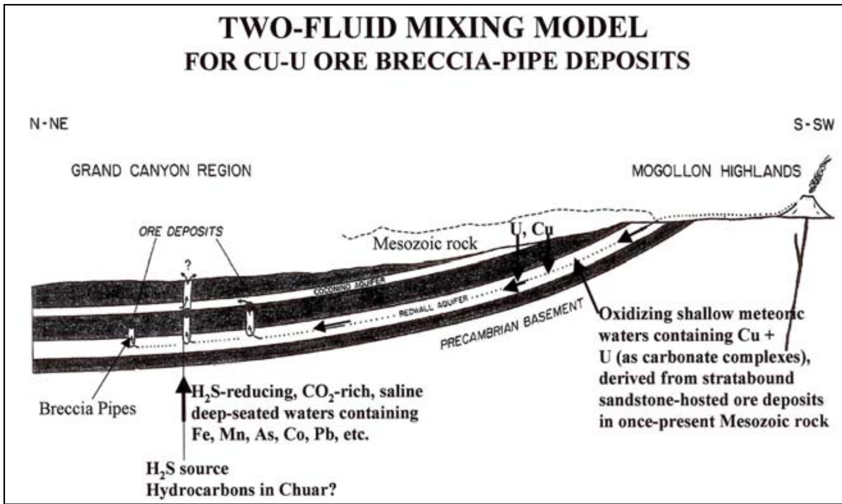

Figure 3. A two-fluid mixing model for the origin of the Cu-U ore deposits in Grand Canyon breccia pipes. It is proposed that the copper and uranium derived from stratabound-hosted ore deposits present in overlying Mesozoic rock before it was eroded away, and that the source of reductant was hydrocarbons in the Precambrian basement. The breccia pipes acted as structural traps for the mixing of these two fluids. Modified from Huntoon (1996).

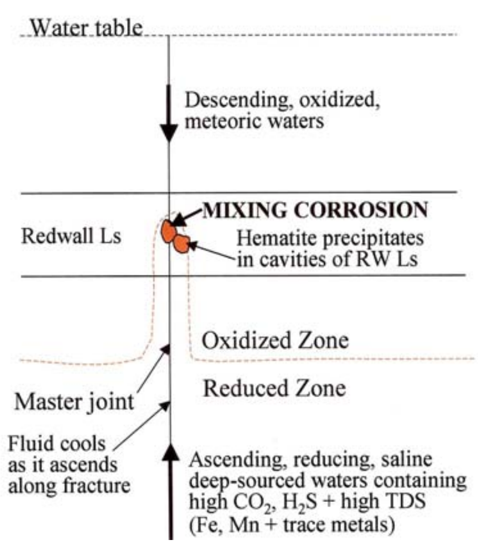

Figure 4. Geochemistry of the hematite episode. The mixture of low TDS, low CO_2 meteoric waters with high TDS, high CO_2 deep-sourced waters creates a solution that dissolves limestone in the mixing zone of these two types of waters. This dissolution process is called "mixing corrosion."

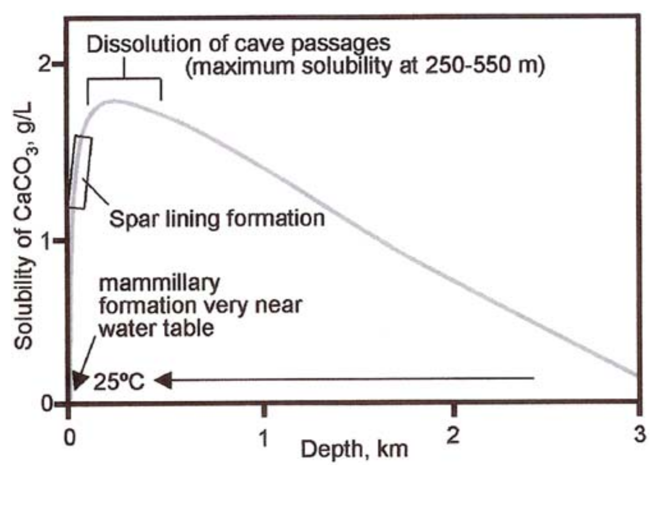

Figure 5. As convective water rises and cools, the solubility of calcite increases so that caves dissolve in the "solutional zone" at ~250-550 m depth. As the water table descends, caves are shifted into the "depositional zone" so that calcite spar lines these cave passages. Mammillary formation occurs very near the water table due to rapid CO_2 loss there. After Dubylansky (1995, 2000).

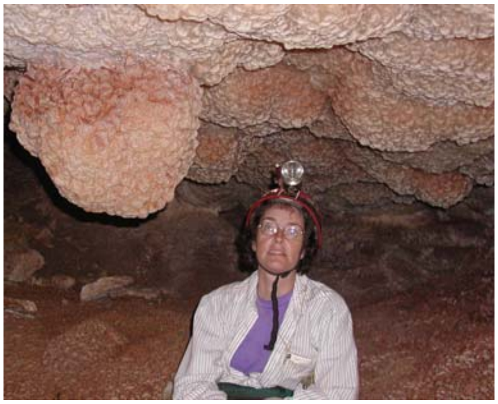

Figure 6. Calcite spar linings covering the ceiling, walls, and floor of Diamond Cave. Photo by Bob Buecher.

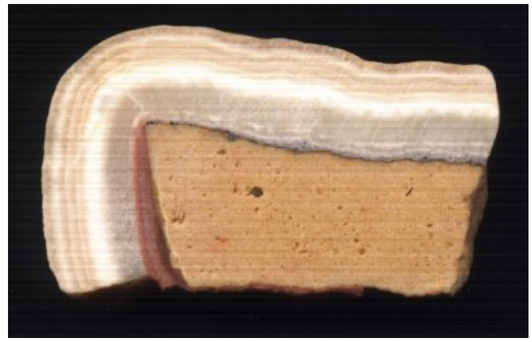

Figure 7. Cross-section of mammillary coating over bedrock, collected from Mother Cave. The mammillaries are composed of microcrystalline fibrous calcite, well suited for dating.

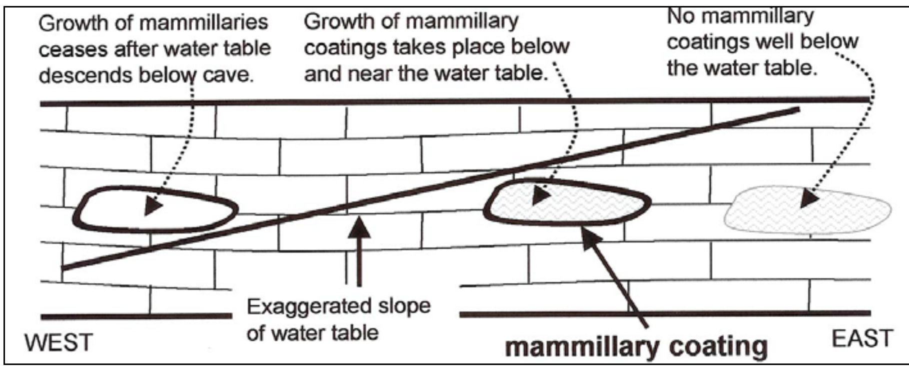

Figure 8. Mammillary coatings form near the water table where there is a rapid degassing of CO_2. After the water table descends through the cave, the coatings no longer grow but are well-preserved in the cave environment.

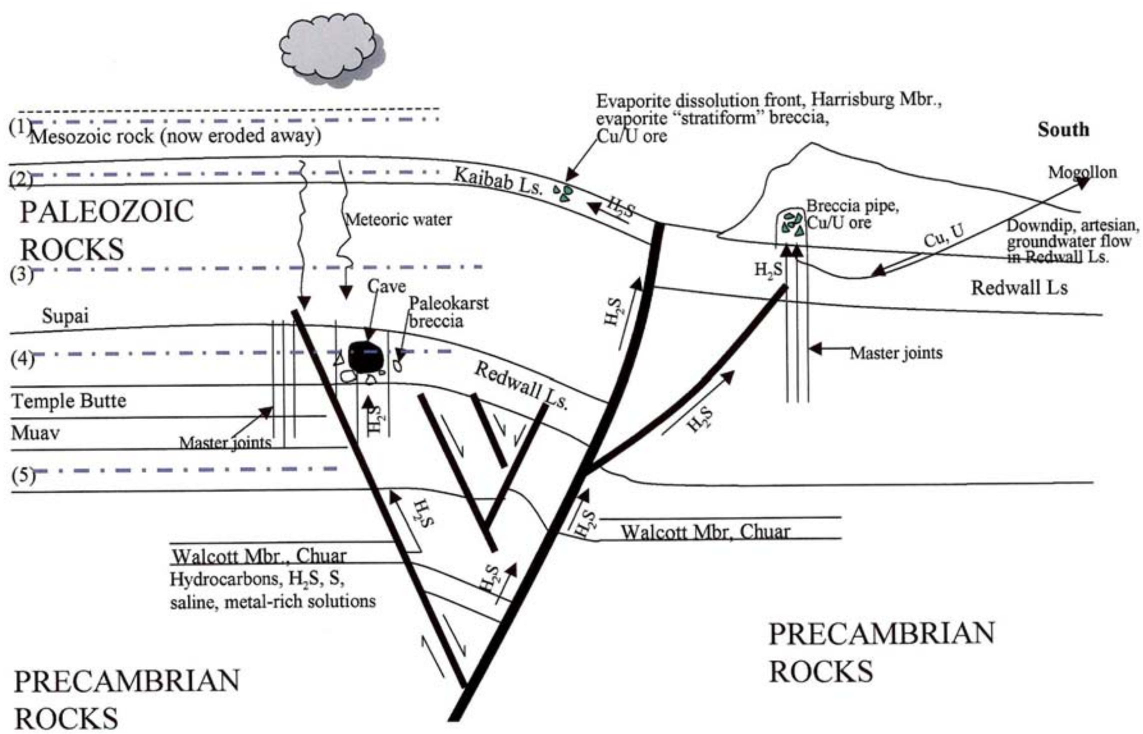

Figure 9. Idealized diagram of the progressive lowering of the water table over time in the Grand Canyon with respect to the different kinds of mine and cave deposits. (See text for explanation).