Preliminary Evidence from Grand Canyon Caves and Mines for the Evolution of Grand Canyon and the Colorado River System

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Abstract: $^{40}Ar/^{39}Ar$ dating of the mine minerals alunite and jarosite, and U-series and U-Pb dating of cave minerals and speleothems have the potential for determining the position of the paleowater table and thus the history of downcutting of the Colorado River system. Also, other data on cave and mine deposits can give information about the processes that have operated in Grand Canyon during its geologic history.

Caves and mines in Grand Canyon are important to understanding the geologic evolution of the Colorado River system. They preserve in their mineralogic and geologic features a record of the descent of the regional water table and thus a history of downcutting in Grand Canyon. These deposits can also supply important information about the geologic history of processes and events in Grand Canyon. Mines of the Grand Canyon region visited during this study include the Grandview Mine, Kaibab Trail barite site, Riverview Mine, the Anita mines (Copper Queen Mine, Northstar prospects, Emerald Mine, Eaststar prospects), Ridenour Mine, Grand Gulch Mine, and Savanic Mine. Caves visited in the region include the Cave of the Domes, Tse'an Bida, Tse'an Kaetan, Grand Canyon Caverns, Bat Cave, and Moria Cave (Figure 1).

Methods of Analyses

A number of analytical methods were performed on various types of mine and cave samples in order to obtain information that might relate to the downcutting and history of Grand Canyon. $^{40}Ar/^{39}Ar$ dating was performed on the minerals alunite and jarosite; U-series ($^{230}Th/^{234}U$ thermal ionization mass spectroscopy) dating on speleothems; and fission-track dating on calcite spar. Stable-isotope analyses were performed on a variety of samples: $\delta^{34}S$ on gypsum, alunite, barite, and native sulfur; $\delta^{13}C$ and $\delta^{18}O$ on mine, cave, and fault calcite-spar; δO_{SO4}, δO_{OH}, and δD_{OH} on alunite; and $^{87}Sr/^{86}Sr$ on cave calcite-spar. X-ray diffraction, electron microscopy, and multielement chemical analyses were also performed on various mineral samples from the caves and mines.

Basic Data

Alunite and Jarosite

The minerals alunite, $KAl_3(SO_4)_2(OH)_6$, and jarosite, $KFe_3(SO_4)_2(OH)_6$, are important for two reasons. First, because these minerals contain potassium, they can be dated by the $^{40}Ar/^{39}Ar$ method (McDougall, 1999). Second, four different stable-isotope values can be determined in these minerals: sulfur in SO_4, hydrogen in OH, and oxygen in OH and SO_4. These stable-isotope values not only can be used to differentiate between supergene and magmatic alunite and jarosite, but they can also indicate the temperature and character of the mineral-forming water (Rye and others, 1992). The low pH and high P_{O_2} needed to form jarosite limits its precipitation to the vadose zone above the water table, while alunite precipitates by reaction of acid-sulfate waters at or near the water table (Rye and Alpers, 1997). Thus, by dating these two minerals, it should be possible to trace the descent of the paleowater table over time.

We have obtained a preliminary $^{40}Ar/^{39}Ar$ step-heating date of 0.56 ± 0.03 Ma for one sample of Grandview Mine alunite. Stable-isotope values for this same alunite ($\delta^{34}S$ = –7.4‰, δD= –85‰, $\delta^{18}O_{OH}$ = +9.3‰, $\delta^{18}O_{SO4}$ = +6.7‰, $\delta^{18}O_{SO4-OH}$ = –2.6‰) demonstrate that it had a

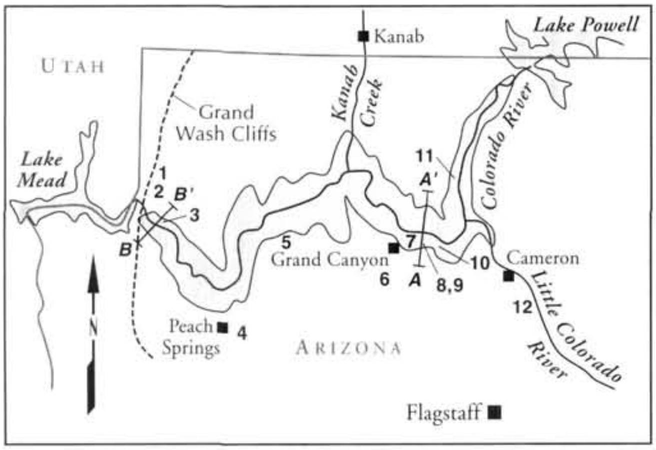

Figure 1. Location map for all the places mentioned in the text: (1) Grand Gulch Mine; (2) Savanic Mine; (3) Bat Cave; (4) Grand Canyon Caverns; (5) Ridenour Mine; (6) Anita mines; (7) Kaibab Trail barite site; (8) Cave of the Domes; (9) Grandview Mine; (10) Tse'an Bida Cave; (11) Moria Cave; (12) Riverview Mine. Cross sections A-A′ and B-B′ correspond to those in Figure 3.

low-temperature (~20 to 30°C) origin likely related to the water table, rather than a magmatic origin. The Savanic Mine jarosite is currently being $^{40}Ar/^{39}Ar$-dated.

Calcite Spar

Three associations of calcite spar have been encountered in this study: (1) spar lining the walls of caves, (2) spar associated with ore mineralization in the mines, and (3) spar filling normal faults. Depleted oxygen-isotope values for 13 spar samples ($\delta^{18}O$ = –9.87‰ to –19.4‰) signify that all three types of spar probably formed from low-temperature (<100°C) hydrothermal solutions. A $^{87}Sr/^{86}Sr$ determination on a calcite-spar wall lining collected from Tse'an Bida Cave measured 0.713593 ± 0.00027. This relatively high ratio (compared to limestone, ~0.708; Faure, 1986) indicates that the water out of which this cave-spar lining precipitated was not in equilibrium with marine limestone. Fission-track dating of calcite spar from the Orphan and Havasu Falls Mines proved unsuccessful.

Calcite-Aragonite Speleothems

Speleothems are secondary mineral deposits that form in caves. Some speleothems, like large hydrothermal calcite-spar crystals form in the phreatic zone, but most (like stalactites and stalagmites) form in the vadose (air-filled) zone. Others, like mammillaries and clouds, form at or near the water table in the shallow-phreatic zone (Hill and Forti, 1997). Thus, by obtaining absolute dates on such types of speleothems, the relative age and position of a preexisting water table can be estimated.

Three U-series dates have been obtained on speleothems collected from Grand Canyon caves: (1) $432^{+38}/_{-30}$ ka date on an aragonite stalactite from Bat Cave (western Grand Canyon); (2) >500 ka date on a calcite mammillary from Tse'an Bida Cave (eastern Grand Canyon), and (3) >500 ka date on a calcite mammillary from Grand Canyon Caverns (near Peach Springs). Future U-Pb dates on the mammillaries, if successful, could place more precise constraints on the position of the water table with respect to time. A U-Pb date on the calcite-spar sample from Moria Cave (northeastern part of Grand Canyon) could also provide a minimum age for early phreatic cave development.

Sequence of Events in Grand Canyon Caves

All of the caves visited in the Grand Canyon area are developed in the Mooney Falls Member of the Redwall Limestone, with the exception of Bat Cave, which is developed in the Kanab Canyon Member of the Muav Limestone. The phreatic caves of Grand Canyon (i.e., "basin karst caves" of Huntoon, 2000) display the following general sequence of deposits and events: (1) an iron-rich (hematite or goethite), metal-enriched, earthy layer; (2) hydrothermal calcite spar linings; (3) replacement gypsum wall rinds/floor blocks; and (4) late-stage speleothems. This entire sequence has been found in Tse'an Bida and Moria Caves, the last three in Tse'an Kaetan Cave (not shown in Figure 1), and the last two in the Cave of the Domes, Grand Canyon Caverns, and Bat Cave.

The iron-rich material in Tse'an Bida Cave was X-rayed and found to be composed of hematite and minor halite; the material in Moria Cave is composed of goethite. These X-ray patterns showed no trace of quartz or clay minerals such as would be expected if these deposits had formed as clastic remnants from the Surprise Canyon Formation or other overlying formations, or had been washed in as vadose sediments. Also, this material is enriched in Mn and contains anomalous As, Ba, Co, Cr, Cu, Fe, Ni, Pb, Sr, V, and Zn—similar (except for uranium) to the metal enrichment found in the mines of Grand Canyon (Wenrich, 1985).

Replacement Gypsum

Gypsum wall-crusts/rinds occur in all of the Grand Canyon caves visited so far; in addition, small gypsum floor blocks were found in Grand Canyon Caverns. As indicated by the sulfur isotope analyses (Figure 2), this cave gypsum formed by a sulfuric acid mechanism as a replacement of limestone; i.e., this gypsum is speleo*genetic* in origin. It is not speleo*themic* gypsum derived from evaporites in the overburden. Evaporites in overlying Mississippian to Triassic rock have sulfur isotope values of $\delta^{34}S$ = +10‰ to +25‰ (Faure, 1986; Figure 2). Therefore, the cave gypsum ($\delta^{34}S$ = –11.0‰ to +5.8‰, CDT) could not possibly have come from a sedimentary source, since little or no fractionation occurs during the simple leaching and reprecipitation of

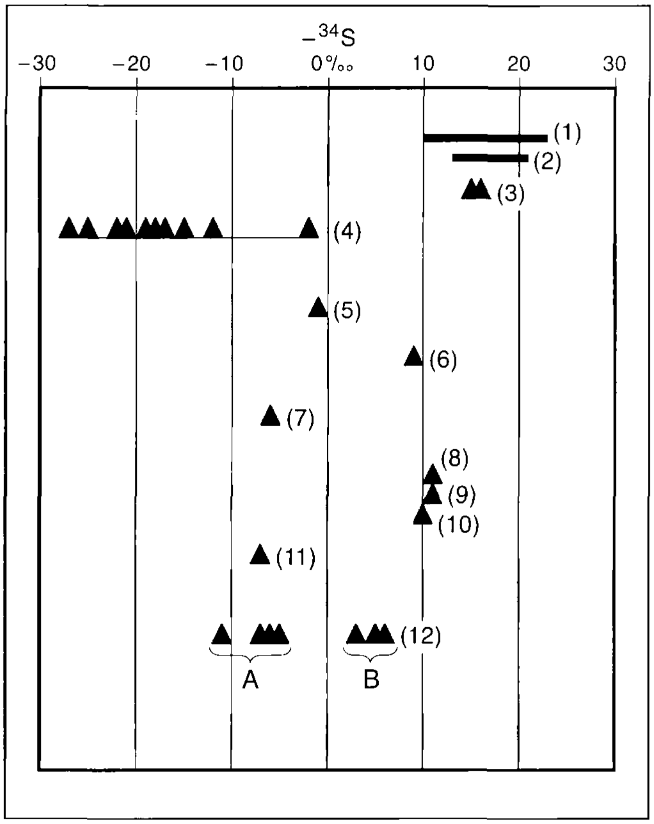

Figure 2. Sulfur isotope data for the various types of deposits in the Grand Canyon region: (1) late Mississippian to Triassic evaporite rock (Faure, 1986); (2) Pennsylvanian-age evaporite rock (Faure, 1986); (3) gypsum evaporite facies in the Kaibab Limestone, South Rim and North Rim (this study); (4) sulfide (pyrite, galena, sphalerite, and chalcopyrite) mineralization, Orphan Mine (Miller and Kulp, 1963); (5) chalcocite, Grandview Mine (this study); (6) pyritic-shale, Walcott Member, Chuar Group (this study); (7) native sulfur, Walcott Member, Chuar Group (this study); (8) barite, Kaibab Trail barite site (this study); (9) barite, Orphan mine (this study); (10) barite, Grandview Mine (this study); (11) alunite, Grandview Mine (this study); (12) cave replacement gypsum (this study), Group A is for South Rim caves in the western Grand Canyon, Group B is for caves farther south (Northstar Mine, Grand Canyon Caverns) and west (Bat Cave). Note that the values for the cave replacement gypsum (12) are isotopically lighter than the sedimentary evaporites in the overburden (1) (2) (3). Therefore the cave gypsum could not have derived from an overlying sedimentary source.

gypsum. The speleogenetic gypsum probably represents a final stage of relatively minor cave dissolution near the water table, and therefore relates to the position of the descending water table in the Grand Canyon region through the late Tertiary.

Discussion of Significance

Some interesting and potentially important results have been obtained regarding the timing of downcutting of the Colorado River system in Grand Canyon, and the relationship of the caves and mines to the geologic history of Grand Canyon.

Timing of Downcutting of Grand Canyon

The absolute dates obtained on the alunite and speleothems relate to positions of the paleowater table, which show how far the Colorado River may have downcut in those regions of Grand Canyon with respect to time. The $^{40}Ar/^{39}Ar$ date and stable isotope values on the alunite from the Grandview Mine suggest that this mineral most likely formed at a low temperature at or just below á perched(?) water table at about 560 ka (Figure 3A-A´). The elevation of the Grandview Mine on Horseshoe Mesa is about 1370 m, and the elevation of the Colorado River in that part of the canyon is about 730 m. The alunite age thus indicates an apparent drop in the water table of no more than 640 m in ~560 ka (assuming a relatively flat water table and not taking into account fault displacement), and places an upper limit on the downcutting rate at ≤1.1 mm/yr. Also, since the Cave of the Domes is at the same level in the Redwall Limestone as the Grandview Mine (Figure 3A-A´), some water table cave development probably occurred at this time on Horseshoe Mesa. Additional dates on Grand Canyon alunite-jarosite samples have the potential to help reconstruct the nature and origin of the paleowater table and rate of downcutting in the same way that Polyak and others (1998) determined the apparent decline of the water table in the Carlsbad Cavern, Guadalupe Mountains, New Mexico area.

The 432 ka date obtained on the aragonite stalactite in Bat Cave is also significant in that it places an upper time limit on the downcutting rate of western Grand Canyon (Figure 3B-B´). The pre–Lake Mead Colorado River was located 332 m below the entrance of Bat Cave (La Rue, 1925). Thus, because stalactites are dripstone deposits that form above the water table, the level of the water table (river level) must have been somewhere below the level of Bat Cave ~0.5 Ma ago, and the rate of downcutting for that part of western Grand Canyon during this time period must have been <0.67 mm/yr. This shows that comparable results can be retrieved from cave dripstone and flowstone as are obtainable from surface travertines. The advantage of studying and dating speleothems is that spelothems are protected from surface erosion and thus are usually better preserved than surface travertines.

The two >500 ka dates on the mammillaries from Tse'an Bida and Grand Canyon Caverns mean that the water table was at cave level in these two caves sometime before 500 ka. Future U-Pb dating of these mammillary crusts has the potential to place important constraints on the position of the water table relative to time. Below-the-water-table speleothems such as mammillaries provide minimum downcutting rates in comparison to above-the-water-table speleothems that provide maximum downcutting rates.

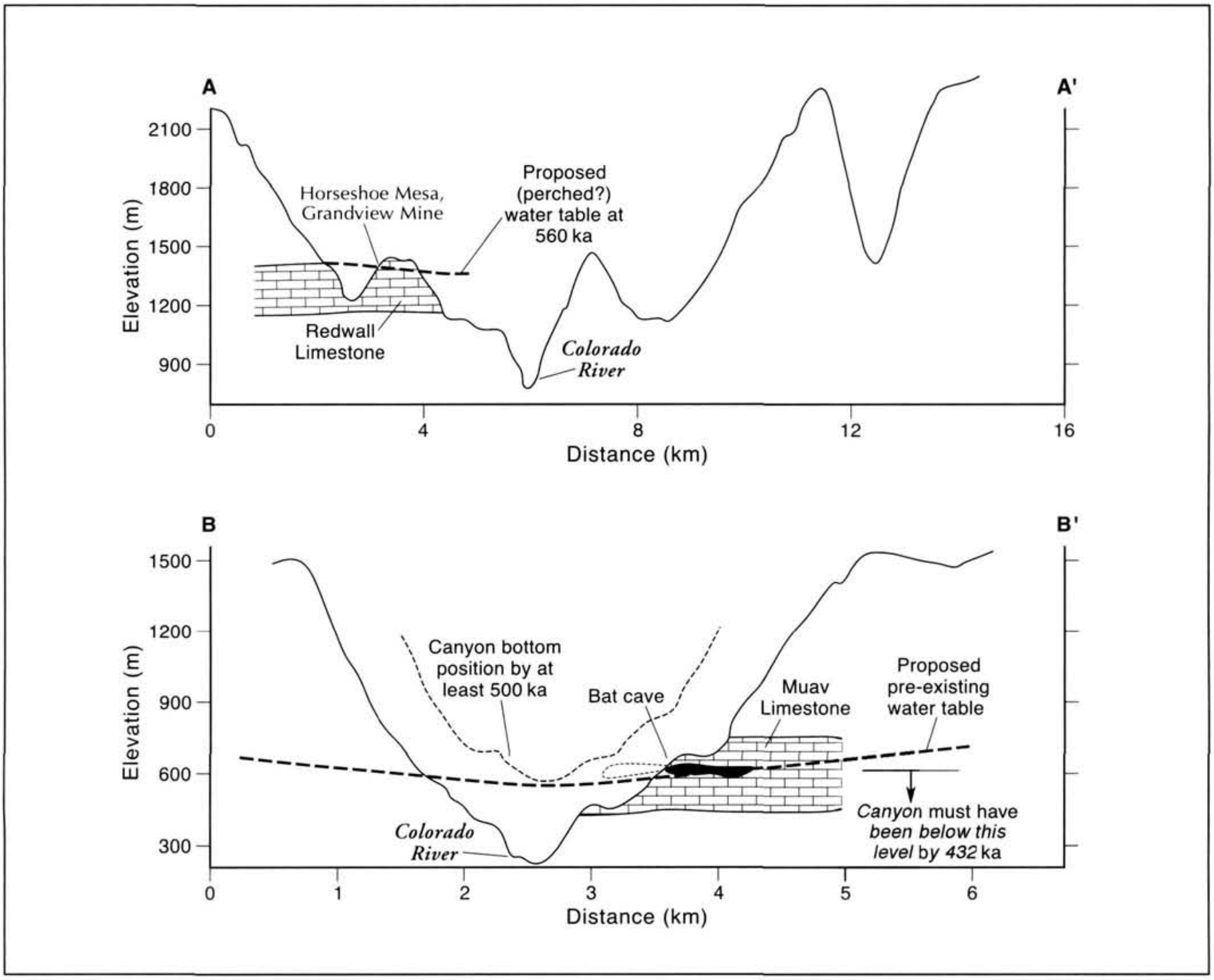

Figure 3. Two cross sections depicting the downcutting of Grand Canyon using data from this study: cross section A-A′, Horsehoe Mesa, eastern Grand Canyon showing proposed water table and canyon profile when the Grandview Mine alunite formed at 560 ka compared to today's profile; cross section B-B in vicinity of Bat Cave, western Grand Canyon showing proposed water table and canyon profile when the Bat Cave stalactite formed at 432 ka compared to today's profile. Canyon profiles from Maptech's Terrain Navigation program

Mines, Caves, and Geologic History of Grand Canyon

Cave and mine deposits in Grand Canyon not only provide information on the time of downcutting by the Colorado River, but they also provide information on the overall geologic history of the canyon. For example, the detailed isotopic study of mineral deposits in mines such as K- and Fe-aluminum sulfates (e.g., alunite and jarosite) and possibly Mn-oxides can yield—besides information related to the water table position—significant information related to the depositional environment. Speleothems not only can give information on maximum and minimum downcutting rates, but they can also give information on climate changes over time. Cave sediments can provide paleomagnetic information and also information on the phreatic and vadose history of events in the canyon. Stable-isotope data from cave and mine deposits can help provide information on the temperature and source of fluids out of which the deposits formed. All of these kinds of data relate to the different processes that have been operative in Grand Canyon over geologic time.

An example of how such data may affect interpretations of processes is our sulfur isotope data on the gypsum rinds in Grand Canyon caves (Figure 2). Since these sulfur isotope values do not match those of sedimentary sulfates (Figure 2), it implies that this cave gypsum had its origin in the migration of H_2S from hydrocarbons in the subsurface, as has been described by Hill (1990) for the caves of the Guadalupe Mountains, New Mexico. Although the data are very preliminary at this time, note in Figure 2 that the sulfur isotope values of the cave gypsum (Group A for South Rim caves in eastern Grand Canyon) and Grandview Mine alunite are almost identical to native sulfur in the hydrocarbon-rich Walcott Member of the Kwagunt Formation (Proterozoic Chuar Group) in eastern Grand Canyon. This correlation may imply that the hydrocarbon source of H_2S for the native sulfur in the Walcott was the same as that for the replacement gypsum in the South Rim caves, and that migration of this H_2S from the Walcott has taken place over time via monocline (stratigraphic), fault, or master-joint avenues of ascent. This migration of H_2S from hydrocarbons may further be related to the source of reduced sulfur for the sulfide and uranium mineralization in the mines of Grand Canyon, a major enigma that has puzzled mine geologists for decades.

Conclusion

This study of caves and mines in Grand Canyon is just beginning. Future work should help determine the age of the Colorado River system and shed light on the geologic history of Grand Canyon.

Acknowledgments

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