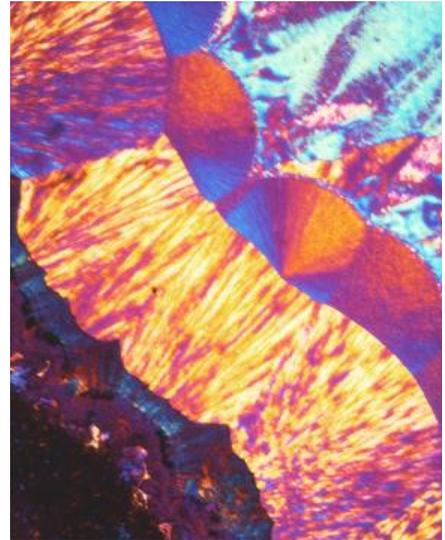


Symposium on Agate and Cryptocrystalline Quartz



September 10 – 13, 2005
Golden, Colorado



Sponsored by Friends of Mineralogy, Colorado Chapter;
Colorado School of Mines Geology Museum;
and U.S. Geological Survey

Cover Photos

{top left} Fortification agate, Hinsdale County, Colorado, collection of the Geology Museum, Colorado School of Mines. Coloration of alternating concentric bands is due to infiltration of Fe with groundwater into the porous chalcedony layers, leaving the impermeable chalcedony bands uncolored (white): ground water was introduced via the symmetric fractures, evidenced by darker brown hues along the orthogonal lines. Specimen about 4 inches across; photo Dan Kile.

{lower left} Photomicrograph showing, in crossed-polarized light, a rhyolite thunder egg shell (lower left) a fibrous phase of silica, opal-CT_{LS} (appearing as a layer of tan fibers bordering the rhyolite cavity wall), and spherulitic and radiating fibrous forms of chalcedony. Field of view approximately 4.8 mm high; photo Dan Kile.

{center right} Photomicrograph of the same field of view, but with a 1λ (first-order red) waveplate inserted to illustrate the length-fast nature of the chalcedony (yellow-orange) and the length-slow character of the opal CT_{LS} (blue). Field of view about 4.8 mm high; photo Dan Kile.

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Symposium on Agate and Cryptocrystalline Quartz

Program and Abstracts

September 10 – 13, 2005

Editors

Daniel Kile

Thomas Michalski

Peter Modreski

Held at Green Center, Colorado School of Mines
Golden, Colorado

Sponsored by

Friends of Mineralogy, Colorado Chapter
Colorado School of Mines Geology Museum
U.S. Geological Survey

Meeting Chairs

Paul Bartos, Colorado School of Mines

James F. Hurlbut, Denver Museum of Nature and Science

Daniel Kile, U.S. Geological Survey

Thomas Michalski, U.S. Geological Survey

Peter Modreski, U.S. Geological Survey

Graphic Designer and Assistant to the Editors
Jeannine Honey

Program

Friday, September 9

7:00 p.m. Welcoming reception, Colorado School of Mines Geology Museum

Saturday, September 10

7:15 – 8:15 a.m. Registration

8:20 Opening remarks – Paul Bartos, Curator, CSM Geology Museum

Morning session I - chair, Paul Bartos, Colorado School of Mines

8:30 – 8:50 The nomenclature of crystalline, cryptocrystalline, and non-crystalline phases of silica - Daniel Kile

8:55 – 9:15 Agates: banding and beyond - Roger K. Pabian

9:20 – 9:40 The beauty of banded agates - Michael R. Carlson

break 9:45-10:05

Morning session II – chair, Pete Modreski, U.S. Geological Survey

10:05 – 10:25 The agates and geodes of northern Chihuahua, Mexico - Brad L. Cross

10:30 – 10:50 Quartz family minerals (agate and amethyst) from Rio Grande do Sul, Brazil, and Uruguay - Rock Currier

10:55 – 11:15 Clovis culture quarry sources and long distance movement of cryptocrystalline lithic material on the great plains - Steven R. Holen

lunch break 11:20 – 1:00

Afternoon session I – chair, Tom Michalski, U.S. Geological Survey

1:00 – 1:20 p.m. Thundereggs: distribution and geologic setting - John Stockwell

1:25 – 1:45 Chalcedony occurrences in the central Great Plains - Roger K. Pabian

1:50 – 2:10 Australian agates and thunder eggs: why one is never enough - Penny Williamson

break 2:15 – 2:35

Afternoon session II - chair, Paul Bartos, Colorado School of Mines

2:35 – 2:55 The Khur agate field, Central Iran - Maziar Nazari

3:00 – 3:20 Fluid inclusion analysis and manganese-iron oxide mineralogy of quartz-chalcedony geodes from the Parana basalts, Rio Grande do Sul, Brazil - Virgil W. Lueth and Philip C. Goodell

3:25 – 3:45 Seven causes of color in banded agates – Thomas C. Michalski and Eugene E. Foord (deceased)

3:50 – 4:10 Very-high-temperature, closed-system origin of agates in basalts: a new model, new and old evidence - Enrique Merino

4:15 – 4:35 Stratigraphic distribution, environments of deposition, and formation of agate in the Buck Hill Volcanic Series, Brewster County, Texas - Andy Zarins

break 4:40 – 4:50

4:50 – 5:30 Idar-Oberstein and its agate history - Renate Schumacher

5:35 end of session

6:00 Social “hour” at CSM Student Center

6:30 Banquet, CSM Student Center; Banquet Presentation: A history of Scottish agates - Brian Jackson

Sunday, September 11

- 8:00 a.m. Opening remarks – Dan Kile, U.S. Geological Survey
Morning session I - chair, Dan Kile, U.S. Geological Survey
- 8:05 – 8:25 Fairburn agate: occurrence in the badlands, grasslands and Black Hills of southwestern South Dakota and northwestern Nebraska - Roger Clark
- 8:30 – 8:50 An American view of Scottish agates - Dale G. Wheeler
- 8:55 – 9:15 Structures and micro-structures in Scottish agates - Brian Jackson
- 9:20 – 9:40 Silicification of fossil wood - Richard Dayvault
- break 9:45 10:05*
- Morning session II – chair, Tom Michalski, U.S. Geological Survey**
- 10:05 10:25 Fluorescence of cryptocrystalline quartz and opal - Peter J. Modreski
- 10:30 – 10:50 Uraniferous opal, Virgin Valley, Nevada, contains evidence of its age and origin – Robert A. Zielinski
- 10:55 – 11:15 Basal (c) face quartz, its history and occurrences - James F. Hurlbut
- lunch break 11:20 – 1:00*
- Afternoon session I – chair, Jim Hurlbut, Denver Museum of Nature and Science**
- 1:00 – 1:20 p.m. Phenomena in agate: clues to its formation? - Si and Ann Frazier
- 1:25 – 1:45 The blue agate of Kittitas County, central Washington - Paul W. O. Hoskin
- 1:50 2:10 Chalcedonies and jaspers used for carving - Helen Serras-Herman
- break 2:15 – 2:35*
- Afternoon session II - chair, Dan Kile, U.S. Geological Survey**
- 2:35 – 2:55 Thinking about thundereggs: An historical sketch of inquiry into their nature and origin - John Stockwell
- 3:00 – 3:20 Ancient agate lore and early efforts to explain agate formation - Robert Proctor
- 3:25 – 3:45 A review of "An Elementary Treatise on Quartz and Opal" by George William Traill, 1870 - Beth Simmons
- 3:50 – 4:10 Chalcedony and unusual habits of crystalline quartz from carbonate concretions in the Alberta badlands - Mike Menzies
- 4:15 – 4:35 Unusual quartz crystal growth habits - Jack Thompson
- break 4:40 – 4:50*
- 4:50 – 5:30 Creede sowbelly agate: banded amethystine quartz and chalcedony - Ed Raines
- 5:35 End of session

Monday, September 12

- 8:00 a.m. Field trip to the Patch Mine ("Glory Hole"), Central City, Gilpin County, Colorado; Dan Kile, USGS (Emeritus)

Tuesday, September 13

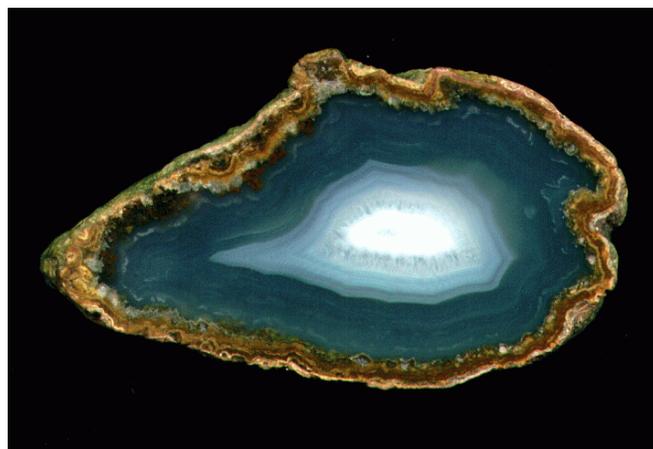
- 8:00 a.m. Field trip to North Table Mountain, Golden, Jefferson County, Colorado; Pete Modreski, USGS

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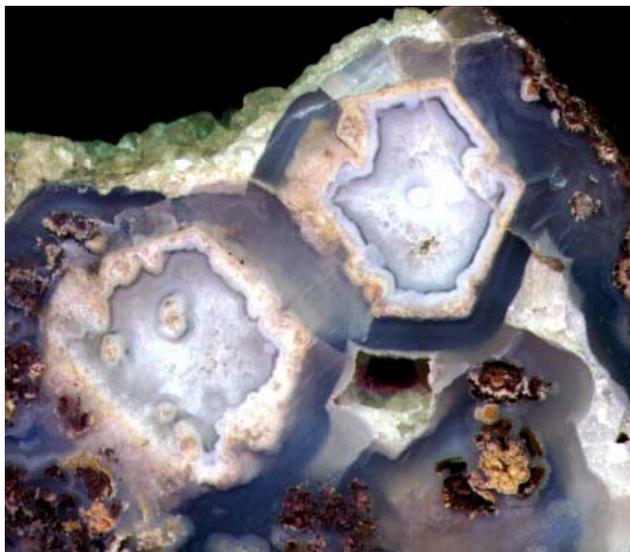
An agate nodule with a very thick limonite crust. Specimen measures 51x45 mm. Figure 6, Nazari, this volume.



Inky blue agate. Specimen measures 52x32 mm. Figure 19, Nazari, this volume.



Brown pigments of siderite in chalcedony bands. Specimen measures 39x31 mm. Figure 29, Nazari, this volume.



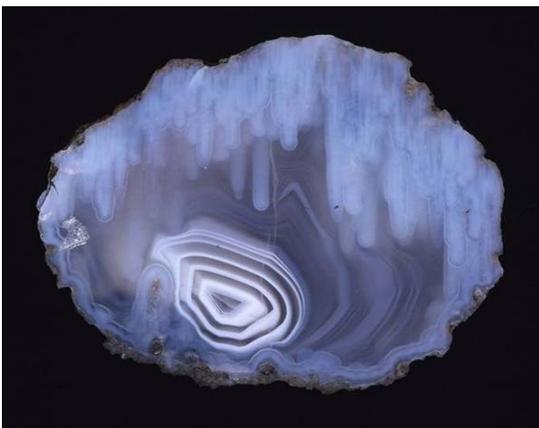
Pseudo-hexagonal crystals of aragonite replaced with chalcedony and quartz. Side edge represents 31 mm. Figure 28, Nazari, this volume.



The eroded Devonian lavas near Montrose, between Scurdie Ness lighthouse (top centre) and Usan (bottom left) and the agates characteristic of each locality. Figure 2, Jackson, History of Scottish Agates, this volume.



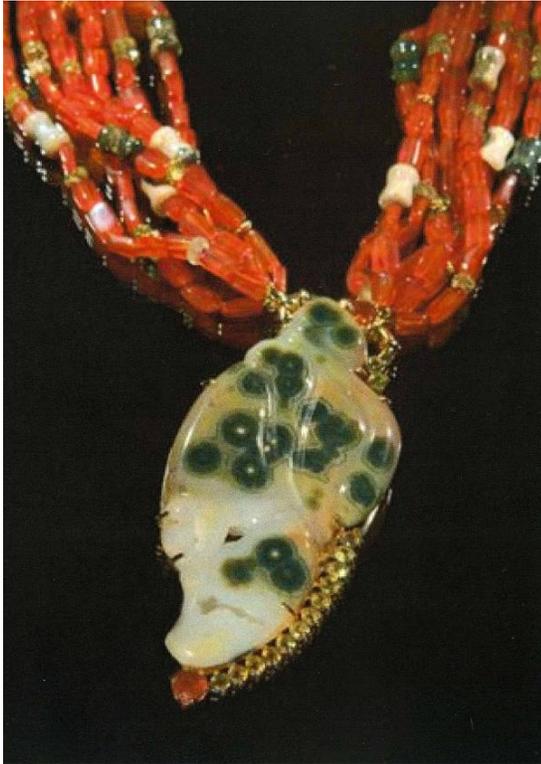
Agate showing many tubes of escape considered by Scottish writers on agates to be central to the explanation of agate formation. Figure 3, Jackson, History of Scottish Agates, this volume.



Gravity controlled stalactites in agate. Figure 4, Jackson, Structures and Micro-Structures in Scottish Agates, this volume.



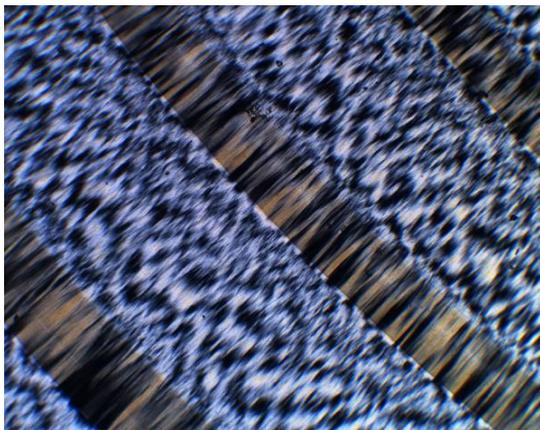
Tube of escape showing band thinning. Figure 5, Jackson, Structures and Micro-Structures in Scottish Agates, this volume.



Carved Jasper, Serras-Herman, this volume.



Agate nodule with red bands. Specimen measures 31x25 mm. Figure 34, Nazari, this volume.



Repetitive alternating chalcedony bands, with fibers twisted and non-twisted: a tremendous case of self-organization. Figure 1, Merino, this volume.



"Rods and cones" texture in Jurassic red wood specimen from Moab, Utah. Width of view approximately 3 mm. (© Daniels 2005). Figure 2, Dayvault, this volume.



This huge cut and polished agate, which is 24 inches across, displays some of the range of colours of the Agate Creek agates. Williamson, this volume.



Agate nodule from Idar-Oberstein with amethyst and pseudomorphs. Figure 2, Schumacher, this volume.



Condor agate showing primary and secondary coloration, Michalski, this volume.

The Nomenclature of Crystalline, Cryptocrystalline, and Non-Crystalline Phases of Silica

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Chalcedony and opal are familiar terms to many as being forms of crystalline and amorphous SiO_2 . There is, however, a wide range of structural states and textures of silica that extend beyond these commonly recognized species. Varieties such as lussatine, quartzine, lussatite, and moganite are forms of silica that are less familiar to mineral collectors, and yet they are frequently encountered in many rocks. The less commonly recognized varieties are defined by differences in the degree of crystallinity (evidenced by X-ray diffraction patterns) and optical properties.

Silica, SiO_2 , can occur naturally in a wide range of structural forms, ranging from ordered silica tetrahedrons to disordered and non-crystalline (*i.e.*, amorphous) silica with variable hydration. For example, although common opal, a hydrous phase of SiO_2 , is generally thought of as an amorphous material with no crystalline structure (as is usually given in standard textbooks), in fact it can vary from non-crystalline to microcrystalline, *i.e.*, it can exhibit a continuum of structure ranging from amorphous (*e.g.*, precious opal, or opal-A_G) to an ordered crystalline material (opal-CT). Identification of these phases can be by visual means, but more often, optical and X-ray methods are necessary to fully characterize the structural and textural state, and hence, assign a correct name to the mineral.

For crystalline silica phases (*i.e.*, phases showing a distinct X-ray pattern), aspects of texture and grain size are defined by terms such as cryptocrystalline, microcrystalline, and micro quartz. Flörke *et al.* (1991) define microcrystalline as a “polycrystalline microstructure of individual crystallites which can only be resolved microscopically (PLM [polarized light microscopy], SEM [scanning electron microscopy] or TEM [transmission electron microscopy]).” However, because of the wide range of magnification inherent between PLM and SEM methods, discrepancies in terminology can arise from this definition. Most geological dictionaries and textbooks (*e.g.*, Thrush, 1968; Sinkankas, 1966; Rice, 1954) define cryptocrystalline by the limit of resolution of individual crystallite properties in a light microscope, and equate the terms microcrystalline and cryptocrystalline. In contrast, Klein and Hurlbut (1999) define cryptocrystalline, but not microcrystalline, as being unresolvable in the light microscope.

Cryptocrystalline (a term usually synonymous with *microcrystalline*) encompasses both fibrous and granular textures, and refers to a phase wherein the grains are too small to resolve with a light microscope. Fibrous textures are exemplified by *chalcedony* (a microcrystalline quartz with a variable water content, *e.g.*, agate), although other minerals, such as malachite, are also commonly fibrous. Flint and chert are considered by some as variants of chalcedony, wherein the chalcedony fibers do not show a preferred orientation (Graetsch, 1994), whereas granular textures (referred to as micro quartz, as found in agates) are characterized by “horizontal layers of fine-grained granular crystals” (Graetsch, 1994) which “show a granular structure of strained grains” and undulatory extinction (Flörke *et al.*, 1991).

The microcrystalline phases of silica give distinct and sharp X-ray patterns, indicating a high

degree of crystallinity, although the peaks are somewhat broadened as compared to coarsely crystalline quartz. Microcrystalline phases characteristically include water in the structure, accounting for lower refractive indices and density; water content increases from crystalline phases (*e.g.*, chalcedony, quartzine) to amorphous phases (*e.g.*, opal-A_G). The non-crystalline (amorphous) phases are characterized by a broad X-ray peak centered around the 2θ 22° region (CuK_α).

The nomenclature for these various phases of both cryptocrystalline and non-crystalline varieties of quartz can be both variable and confusing. Accordingly, a synopsis is presented below that summarizes the more commonly encountered classifications and variants of the more notable silica phases. This terminology is based mostly on the works of Flörke *et al.* (1991) and Graetsch (1994).

I. Ordered/crystalline silica; macro-polymorphs of SiO₂

- quartz: occurs in low (α) or high (β) temperature forms; α quartz (low quartz) is hexagonal, crystallizes < 573 °C. and is granular to euhedral with undulatory extinction in thin section. β quartz is hexagonal, bipyramidal, and crystallizes > 573 °C.
- tridymite: crystallizes > 870 °C.; occurs in a variety of polymorphs and polytypes (Gaines *et al.*, 1997), symmetries range from hexagonal to triclinic
- cristobalite: crystallizes > 1470 °C.; occurs in low (α, tetragonal) and high-temperature forms (β, isometric)
- coesite: monoclinic, characteristic palisade texture; forms at pressures > 20 kbar and high temperatures; associated with impact craters or deep metamorphic rocks
- stishovite: tetragonal, formed at high temperature and pressure; also associated with impact craters

II. Ordered/crystalline silica; microcrystalline polymorphs of SiO₂

- moganite = ***lutecite***: monoclinic SiO₂ phase, as thin plates with inclined extinction; approved IMA-CNMMN, 1999. Reported to be far more prevalent than previously thought (Heaney and Post, 1992); occurs as microcrystalline fibrous (length slow) silica lining vesicles or intergrown with chalcedony, where it is indistinguishable from chalcedony in hand specimen (Gaines *et al.*, 1997)
- chalcedony: subparallel fiber bundles, length fast, c-axis perpendicular to fiber elongation; patchy extinction along fibers due to rotation of c-axis (chert = random fiber orientation)
- ***quartzine***: length slow, c-axis parallel to fiber elongation

III. Microcrystalline polymorphs of opal; cristobalite & tridymite stacking partly disordered, short range ordering, interstitial water (and consequently lower indices of refraction relative to the ordered crystalline silicas); brownish in PLM

- opal-C_p, also known as opal C_{LF} = ***lussatine*** (platy, anisotropic)
- opal-C: massy, *i.e.*, a dense, tangled fibrous matrix; optical character of fiber elongation is not measureable
- opal-CT_{LS}: ***lussatite***; common opal; disordered low cristobalite
- opal-CT_M: common opal; ~ isotropic to weakly anisotropic; fine-grained, dense, tangled matrix

IV. Non-crystalline opal

- opal-A: a non-crystalline opal
- opal-A_G: “gel” or precious opal, composed of close packed silica spheres, packing ordered with diffraction effects in precious opal; disordered packing in potch opal
- opal-A_N: hyalite; botryoidal crusts on volcanic or other rocks

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Agates: Banding and Beyond

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Introduction---A survey of published literature about agates reveals that several topics stand out above all others: (1) where to collect agates, with little or no regard to the scientific aspects of agate occurrences; (2) how banded agates formed, and what were the physical and chemical processes involved; and (3) coloring of agates, and the trace elements involved. Few papers deal with other geologic aspects that include but are not restricted to: (1) correlation problems, both local and regional; (2) impacts from comets or asteroids; (3) mass extinctions and biologic crises; (4) Precambrian atmospheres; (5) bacterial origins of features in agates; (6) paleosols, or ancient soil horizons; (7) pH of associated waters. Pabian and Zarins (1994) briefly touched upon several applications that agates may have toward deciphering the geologic history of our planet, and some very fruitful research on agates has been accomplished in the past several decades. A review of some studies that have been made, some first hand observations, and some suggestions for further research follow.

Bands---One of the oldest theories as to the origination of bands deals with silica saturated waters passing through a vesicle and depositing one layer of agate at a time, and over many years, a banded agate results. This idea has long been discarded, and several new and better ideas have been proposed. Keith and Padden (1963, 1964a, 1964b) proposed that impurities of like electrical charges brought about the banding in agates when such impurities settled in the troughs at the tips of spherulitic crystals, and several (hundreds of) successions of this phenomenon occurred. The end product would be a banded agate, and they produced similar results with several different minerals. Landmesser (1995, 1998) proposed that the first bands in an agate formed a skeletal structure and the banding process was completed by “stuffing” this framework with additional silica, and we have examples of agate nodules that appear to be under stuffed and have large hollows that are between parallel but separated bands. That the vesicle may have been filled with silica before the banding proceeded is borne out by a Coyamito nodule from Chihuahua, Mexico, and a Union Road agate from Missouri, where banding exists only in the outer perimeter of the nodules, the interiors being granular rather than fibrous silica. We also have examples of numerous silica spherulites that appear to be coalescing and forming bands in a Luna agate from Chihuahua, Mexico, and an un-named agate from the Permian of Nebraska. The latter specimen may be associated with a thin bed of bentonite. A small agate from the Miocene of west Texas appears to be made up of several, small already banded patterns that are coalescing into one larger pattern. I point these out to suggest that there may be several plausible explanations for the origins of bands in agates, and in future studies of agates, it may be necessary to understand which banding process is being observed.

Agate-like Structures---Agates are not the only mineral that appears in banded forms. An understanding of the bands of agates may be improved upon by having some insight into other minerals that come in banded varieties, including: sphalerite, rhodochrosite, and malachite. Many minerals that come in banded, micro-crystalline forms have been described by Lebedev (1967), a very important Russian paper that appears in English translation by the American Geologic Institute.

Included in this group of agate-like structures are some silica minerals that have been called agate such as Missouri Lace agate, Louisiana agates, agates from Mississippi and Georgia, and African Blue Lace agate. These gems do not appear to have a spherulitic microstructure that is common to other banded agates. It should be pointed out that these gems are usually of marine sedimentary origin, and are associated with dolomite, whereas spherulitically crystallized marine sedimentary agates such as Fairburn or Tepee Canyon agates are associated with limestone. Did magnesium play a role in the microstructure of these kinds of “agate”?

Precambrian atmospheres---Finding the world’s oldest agates may have some implications into learning about Precambrian atmospheres that are thought to have been composed mostly of ammonia and methane until sometime in the late Precambrian. I have observed many examples of conglomerate of Huronian (ca. 2000 mya) age and no gravel clasts of agate have yet been observed in these. A banded agate structure may have been unstable in an acidic, ammonia-methane atmosphere, and agates may have been unable to form until earth acquired an oxygen-nitrogen atmosphere.

Correlation and source area problems---Agua Nueva agates from Chihuahua, Mexico, are commonly characterized by having a bright yellow band about their periphery (Cross, 1996), and collections of Gallego agates from Chihuahua show a banding pattern that repeats itself in many nodules from that area. Knowledge of such banding sequences may prove to be of some value in local correlation of host rock units. The Guernsey Lake agates of Wyoming, and Tepee Canyon agates of South Dakota have been found in marine sedimentary rocks of middle to late Pennsylvanian age, and late Pennsylvanian sediments as far away as eastern Nebraska contain similarly structured agate nodules; that is, an agate nodule in a chert matrix. It is a stretch of the imagination to think that a regional correlation of marine units could be made on the basis of these agates, however.

Moxon (2002) has produced some interesting studies that relate the age of the included agate to the age of the host rock in which it formed by using crystal sizes. Moxon’s work suggested that the agates formed shortly after the host rock. This study is important inasmuch as if there were a great disparity between the age of the host rock and the enclosed agates, the agates would have much less value in correlations.

Paleotemperatures---Fallick, Jocelyn, Donnelly, Guy, and Behan, (1985) have studied the hydrogen and oxygen isotopes in water included in agates from the Devonian of Scotland, and they suggest that these agates formed at relatively low temperatures. Their study was

done on amygdaloidal agates. Similar studies on agates of sedimentary origin and thunder egg agates may yield a much better picture of the conditions and environments in which the various kinds of agates form.

Organic components in agates---Hofmann (1999) has suggested that some filamentous structures and inclusions in agates may be of microbial (bacterial?) origin. He showed examples of plume agate from California as being a possible representative of organic material in agate. Similar structures in thunder eggs from Oregon were studied by Brown (1956). A small agate nodule from the Triassic of Nova Scotia has several layers of limonite that appear to be curled as algae does in dried out ponds. These kinds of structures are commonly observed in water wells of the Dakota Formation in much of Nebraska. They are formed by anaerobic bacteria that cause iron oxides to be deposited on pumps and casings in wells, and are cause for considerable water well maintenance.

Impact structures---Kinnunen and Lindqvist (1998) have shown that agates with a typical “chicken-wire” like fracture pattern are associated with impact structures, and they have traced such agates back to their sources in Finland and have discovered several hitherto unknown extraterrestrial impact sites. They have christened these agates as “pathfinders.” I have an image of an agate from the Ordovician of Wales that has such a fracture pattern, and have suggested to the owning agency of the agate that it might indicate the presence an unknown impact site in or near Wales.

Biologic crises and mass extinctions---The Lake Superior agate that formed in place in volcanic rocks of late Precambrian age are an example of an abundant, widespread occurrence of agates that takes place at about the same time in the earth’s history that there is a considerable change in faunas. During this time, the primitive Ediacaran faunas are giving way to the shelly faunas of the early Cambrian. During the Devonian, the abundant agate resources of Scotland formed at about the same time faunas changed from early to late Paleozoic constituencies. The colonial animals, primitive mollusks and trilobites gave way to echinoderm rich fauna, goniatite mollusks, and many trilobite families perished.

Many of the world’s largest agate occurrences are found the Permian-Triassic boundary, the greatest mass extinction of all time. Many of the agates of Brazil, Germany, Poland, Australia, and South Africa all are products of this time. Agate formation continued on into the Triassic as evidenced by extensive deposits along the eastern seaboard of the US, starting in about North Carolina, and extending northeastward into New Brunswick and Nova Scotia in Canada.

The extensive agate deposits of India are related to the Deccan basalts of late Cretaceous age (Bose, 1908-1909, Officer and Drake, 1985), flows that some researchers think were caused by the late Cretaceous impact that brought about the demise of dinosaurs, ammonites, and hundreds of species of foraminifers. Abundant agate deposits in the Miocene of Texas and Oregon came about at about the same time as important changes in both terrestrial and marine faunas.

Paleosols---Paleosols are fossil soil horizons that show evidence of biotic activity including bacterial activity, root mottling, and development of structures such as pisolites and oolites. Pisolites form in relatively high energy environments where mineral laden waters pass through cavities in rocks or soils and leave deposits of minerals such as calcite, limonite, and goethite. Inclusions of pisolites are common in especially amygdaloidal agates. Many specimens from west Texas and northern Mexico contain pisolites. The presence of agates may be of use in establishing the presence of erosional surfaces and local to regional unconformities.

Conclusions---Agates may have considerable value and application to solving some modern geological problems. They should receive the same attention that is shown to fossils and other minerals and structures in providing evidence for interpretation of the earth's history.

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The Beauty of Banded Agates

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The Beauty of Banded Agates book was designed to demonstrate the visual appeal of agates, and also to give some basic information about them. There have been many fine works about the geology and formation of agates, but there seemed to be a lack of books that show why we usually collect them: because they are incredibly lovely and wondrous works of nature's art.

Most serious collectors prefer the whole or polished halves as specimens, but there are many more people who fashion agates into items such as cabochons. These may or may not be used in the manufacture of jewelry. The book seeks to show the range of how fine agates may be enjoyed in these different ways.

There are far too many types of agates to adequately discuss in a limited space, so the field was narrowed to banded or fortification agates. From there, eight of the world's more beautiful banded agate types were chosen. The author had many examples of them to photograph, and background information could also be obtained about the chosen varieties.

Pete Rodewald and Dennis Westman were enlisted to help with the photography. Both readily volunteered, and Pete was an especially experienced addition to the project, as he had previously won several important mineral photography competitions.

With many fine photos to choose from, the book evolved into a coffee-table format, and the text was shortened to provide more space for the agates themselves. An experienced designer was chosen to lay out the book in an aesthetic manner. The overriding focus remained to promote the beauty of these stones.

The book was divided into the following chapters: About Agates, Agate Quality, Characteristics of Banded Agates, Lapidary, Botswana Agate, Brazilian Agate, Condor Agate, Dryhead Agate, Fairburn Agate, Lake Superior Agate, Mexican Agate, Queensland Agate, Other Banded Agates, and Conclusions

The slides for the program at the agate symposium are taken from the book to reflect some of the main features or characteristics of the agates, and then to show examples of the main type of agates explored. The author will briefly discuss these features and agate varieties, and also show the range of each type in regards to color, pattern, etc.

It should be noted that while most of the agates reviewed are of volcanic origin, there are also two types of sedimentary agates included: Fairburn and Dryhead agates. While these types do not exhibit the range of characteristics seen in the volcanic agates, they are certainly very beautiful varieties in their own unique ways.

The Dryhead and Lake Superior agates pictured in the book were self collected by the author. The current status and production of the agates shown will also be noted. The goal of the program is reflect what is included in the book, and to leave the audience with a renewed enthusiasm for fine-banded agates.

The Agates and Geodes of Northern Chihuahua, Mexico

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Overview

Since the mid-1940's, Mexico has gifted collectors with a wide variety of colorful, complex, and intriguing agates, geodes, and thundereggs. The occurrences are found as isolated deposits, most within andesites, rhyolites, and ash flow tuffs that range in age from 38 to 44 million years old. Rare exceptions, such as Crazy Lace Agate, do occur and can be found in Cretaceous (90 to 65 million years) limestone.

The occurrences are all found in association with past tectonic activity with regional trends of deposits easily observed. Traveling south of El Paso, Texas along Mexican Highway 45, the first commercial quartz geode deposit is found near Villa Ahumada, Chihuahua, approximately 83 miles south of the border. Intermittent deposits of colorful agate nodules and quartz geodes can be traced in a southerly direction into the state of Durango, a distance of at least 450 miles.

A vast majority of the more popular agates (e.g., Agua Nueva, "Coconut" geodes, Coyamito, and Laguna) are concentrated mid-way between El Paso and Chihuahua City in the Sierra Gallego region. A second trend or belt of occurrences continues off to the northwest some 125 miles to the modern-day city of Nuevo Casas Grandes, then 100 miles north up to Palomas on the U.S. – Mexico border and finally back southeast to our starting point, Villa Ahumada.

Each variety of agate is named after a nearby ranch or railroad station and all are found on private land, usually large cattle ranches. Although quality material could be easily collected from the land surface in the 1940's and 1950's, loose material quickly disappeared and hard rock mining was initiated. Mexican mining law establishes that all minerals are owned by the Republic; however, private parties may exploit the minerals (except oil, gas, and radioactive minerals) through federally-issued concessions. Exploration concessions are initially granted for six years and exploitation concessions are valid for 50 years. Only Mexican individuals and incorporated companies can be granted a concession. Surface access rights are not granted with the concessions and must be negotiated separately with the landowner. Obligations, including assessment work, payment of mining taxes, and compliance with environmental laws must be maintained in order to retain the concession.

The key to successful agate production within the region is first finding vesicles in the host rock, followed by finding an area where the vesicles are filled with agate, and finally finding an area where there is *good* agate. Although finding a productive area is very difficult, separation of the agate from the host rock can be relatively easy. While heavy equipment must be utilized to break down the host material to manageable size, most of the agates are not tightly bonded to the host rock and can be dislodged with minimal effort.

Although there are many varieties of Mexican agate, each has a unique set of characteristics such as specific color ranges, fineness of banding, nodule size and shape, as well as external

pitting and color that help provide clues in identifying the exact location. A few of the more popular varieties are described below.

Example Varieties

Laguna Agate

This nodular agate is perhaps one of the most popular varieties, recognized by its colorful, distinct, ornate, fluted, and holly leaf-like fortifications. The brighter color combinations are many times found in the central portion of the nodule where clear chalcedony tends to alternate with opaque bands. There are several colors found in Laguna that seem to be particularly typical. Raspberry red, shades of orchid, pleasing soft yellows, orange, and gray bands are especially common. The most prized specimens have contrasting combinations of color such as purple, red, and orange.

Laguna Agates will often demonstrate an optical phenomenon known as “shadow”, an effect of waves and motion created by extremely clear bands of agate alternating and paralleling opaque bands as the agate is rolled about under a light source.

Nodules ranging in size from a hen egg up to a large cantaloupe are mined immediately east of Estación Ojo Laguna in the Sierra El Oso, located approximately 170 miles south of El Paso.

Coyamito Agate

Rare color combinations of purple and yellow, rose and white, as well as various shades of red, orange and mustard are found in this Chihuahuan gem. Unlike the Laguna Agates, most of the brighter colors typically occur in the outer perimeter. The contrasting colors, coupled with ghostly pseudomorphs of evaporitic and zeolitic minerals, make this agate one of Chihuahua’s most prized gems.

Found on Rancho Coyamito Norte, or about 30 miles north of the Laguna Agate deposit, two primary deposits are identified on the ranch. The *Los Alamos* area is the most southerly productive region on the ranch and characteristically contains muted or dark shades of lavender and yellow bands encasing both molds and casts of past mineralization. These agates are particularly large and can reach upwards of a foot in diameter.

Some 500 yards to the north of Los Alamos is *La Sonoreña*, a grouping of small and isolated concentrations of agate. Here, over 20 small pits are found on the slopes of the hills where each pit tends to produce a unique type of agate. Few agates offer the variety and appeal as those from this ranch.

Moctezuma Agate

Pastel shades of salmon, pink, yellow, tan, and white readily identify a Mexican agate locality as Rancho El Barreal. Found east of Estación Moctezuma, these nodules are located within the mining concession Laguna Verde. These nodules typically have a siliceous and sometimes chalky white banana peel-like rind. The phenomenon of chromatography, a separation of coloring agents by semi-permeable bands, appears to have operated many times in Moctezuma Agate to produce abrupt and dramatic color changes.

Apache Agate

Unlike the common fortification pattern found in other nodular agates, Apache agate has bright red, vivid orange, and dark yellow splashes of color seemingly suspended as draped folds and swirling veils in colorless to deep blue chalcedony. Located on Rancho La Viñata, most of the host andesite has succumbed to the attacks of mother nature, leaving the irregular-shaped nodules to prominently stand out in a beige clay-like soil.

Agua Nueva Agate

Occurring in both nodule and vein form, the trademark characteristic for Agua Nueva Agate are remarkable straw-like tubes. Vein agate, reaching over 14 inches in thickness, occurs on Rancho Los Nogales as a golden brown to red moss agate with individual pockets of purple, white, and pink tube agate. The individual tubes average three-quarters of an inch in diameter, many times being completely encased by euhedral quartz. Found within the same mining concession, *Mi Sueño*, nodular banded agates shaded in lavender, purple, gold, and yellow are also found.

A second area of the ranch, claimed under the name *Agua Nueva*, produces nodular agates with a flat base and somewhat domed top. These nodules characteristically contain an outer perimeter of dark yellow to light orange moss agate. The central portion of the nodules typically contains rosy violet hues contrasting with the occasional dark green, black, or white band.

Crazy Lace Agate

Towering above the desert floor to an elevation of 6,200 feet, the Sierra Santa Lucia hosts numerous agate mining concessions and diggings. Primarily occurring as a vein agate, irregular curved and twisted bands in shapes of zig-zags, scallops, bouquets, sunbursts, and eyes compose this agate. The peculiar structures are many times grouped together in a larger spherical complex. While individual bands of red, yellow, orange, or brown occur, the vast majority of the material is gray or white. However, widespread staining is primarily responsible for much of the color.

Unlike all other Mexican Agate, Crazy Lace Agate occurs as an epithermal vein deposit and is mined from a highly siliceous, dark gray limestone of Cretaceous age; however, agate emplacement didn't occur until rhyolitic domes intruded the area some 40 to 50 million years ago during Tertiary time.

"Coconut" Geodes

The popular Mexican "coconut" geodes occur within an ash-flow tuff at Las Choyas, a remote geographic point approximately 22 miles northeast of Ojo Laguna, Chihuahua. These quartz geodes are mined from a two square-mile area and have constituted a multi-million dollar business. Geodes from this location are easily identified by their near-perfect spherical shape. They occur in a 44 million year old ash flow tuff and the geodes, when brought to the surface, appear white from the clinging fragments of the volcanic ash in which they were imbedded. Roughly three-foot diameter shafts are hand dug to depths of 100 feet or more through tenacious, welded ash flow tuff. Once the geode-producing unit is reached, tunnels are constructed in the highly altered tuff, following the pay zone.

Only 20 percent of the geodes are hollow and those that are, usually have an outer wall of variable thickness consisting of blue-gray banded agate. However, the walls of some

coconuts consist of siderite and are termed “brown rimmed coconuts”. The walls grade inward into well-defined crystalline quartz of colorless, smoky, and amethystine varieties. Finally, there is a complex of late-stage sequence of minerals, including carbonates, manganese oxides, and iron oxides and hydroxides, in the centers of many of the geodes.

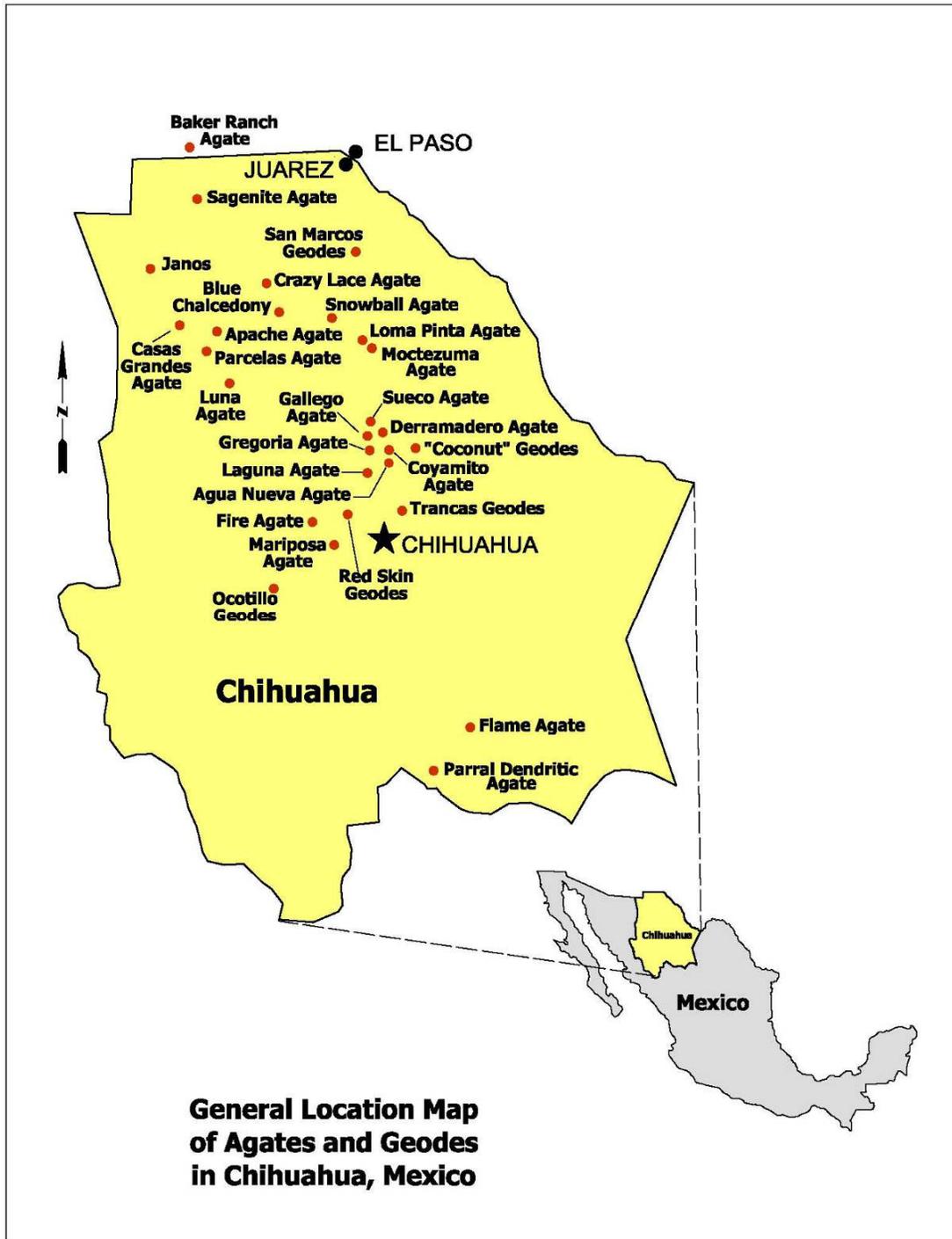
Conclusion

Mexican agates and geodes are ranked among the very finest varieties of cryptocrystalline quartz. Occurring in both nodular and vein forms, a wide-array of types are found including moss, bands, eyes, and tubes. Although occurrences number near one hundred, much of the Mexican republic remains relatively unexplored and new varieties will certainly be discovered in the future.

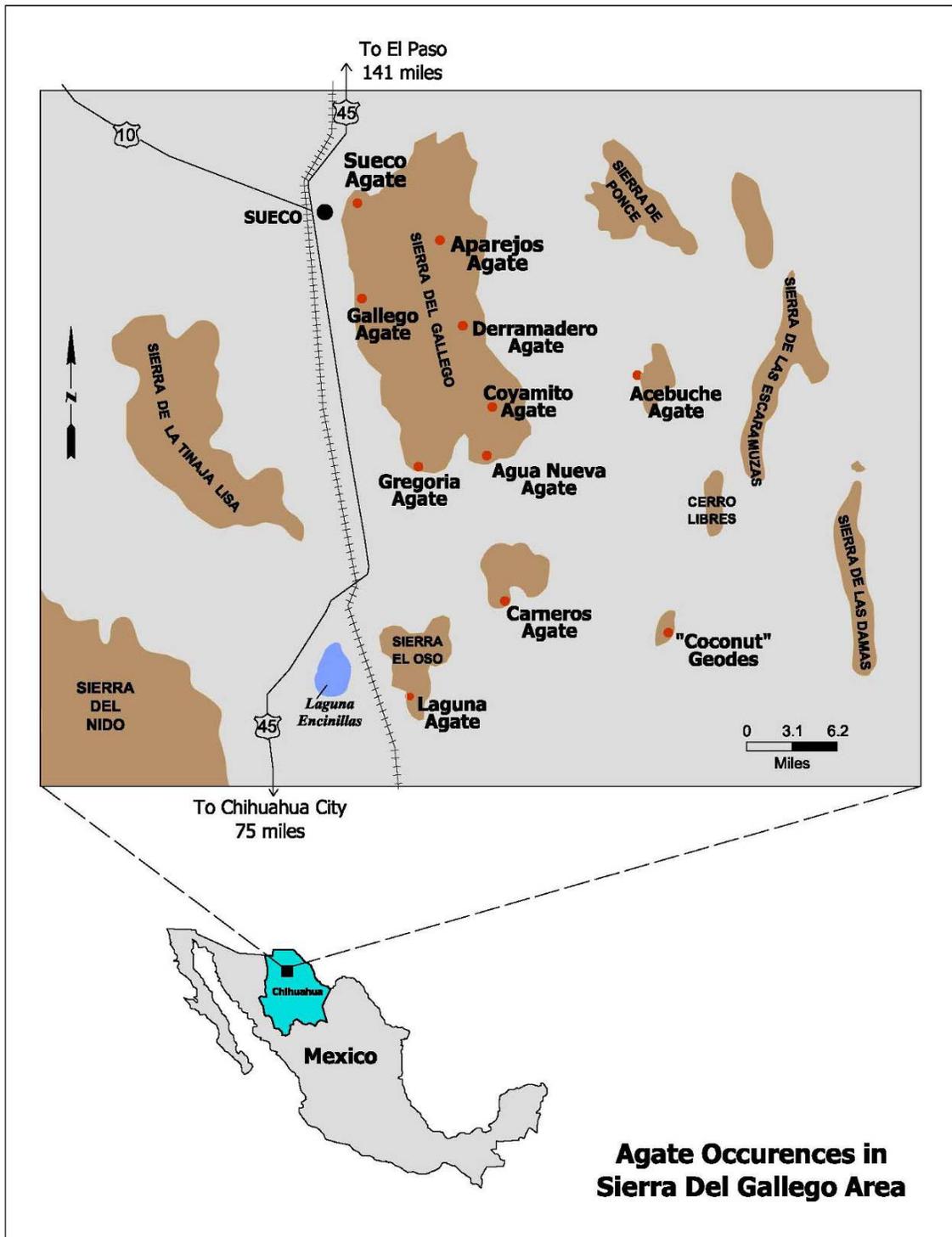
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General Location Map of Agate and Geode Occurrences in Chihuahua, Mexico



Agate Occurrences within the Sierra del Gallego, Chih., Mexico



**Quartz Family Minerals (Agate and Amethyst) from
Rio Grande do Sul, Brazil, and Uruguay**

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The quartz family mineral varieties (agate and amethyst), from Rio Grande do Sul, Brazil, and to a lesser extent those found near Artigas, Uruguay, are among the most commonly encountered in retail natural history sales venues around the world, and their production dwarfs that from any other localities. The production of amethyst geodes from Rio Grande do Sul alone is on the order of two to four megatons a year. In this southernmost state of Brazil, an industry has grown up around the mining and processing of amethyst and agate that shows no sign of slowing down or diminishing. It has outlasted the shoe-making industry there which some years ago moved to China. Although many containers of amethyst and rough agate are yearly exported from Brazil to China, the local cutting and polishing of agate and amethyst items remains robust. The agate and amethyst products produced in Brazil, as they have for many decades, remain the benchmark against which many other prolific gem and mineral localities are measured.

We shall explore the sources of agate and amethyst production in southern Brazil and Uruguay and follow the agate and amethyst as it makes its way to the factories where it is converted to items sold in the retail trade at gem and mineral shows. You will see something of the efficient production methods that are used to cut and polish this material and how it is sold and shipped all over the world.

Clovis Culture Quarry Sources and Long Distance Movement of Cryptocrystalline Lithic Material on the Great Plains

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Sources of high quality lithic material are widely dispersed over the Great Plains with vast areas between containing little or no lithic resources. Clovis groups at the end of the last glacial period, ca. 11,000 radiocarbon years ago, quarried the highest quality lithic materials from bedrock sources. These highly mobile bands moved this lithic material up to 600 km from the quarry source in the form of large bifaces and complete toolkits. Projectile points and preforms have been recorded up to 1,000 km from the quarry source. Movement of lithic material in the range of 600 to 1,000 km appears to be the result of exchange of lithic material between band groups. The high mobility of these early hunter-gatherers appears to be an adaptation to climate change and the new Holocene environment.

Some exotic lithic materials, for example quartz crystal, appear to have been quarried for reasons other than to produce purely functional tools. Exotic lithic materials were often cached for a variety of reasons.

Thundereggs: Distribution and Geologic Setting

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Thundereggs (expanded spherulites and lithophysae, whether considered variations of one structure or to have differing genetic histories) provide a locus for the deposition of agate and other forms of cryptocrystalline quartz. Thundereggs, in contrast to geodes (Keokuk or Brazilian types), develop in silicic volcanic rocks, usually rhyolites, in either the perlitic portion of flows and domes or the vitrophyric portions of welded tuffs, although there is controversy as to whether they form in flows only or in both flows and welded tuffs. Rhyolitic rocks are found on all continents, but thundereggs, probably reflecting their relatively low commercial value, are generally not reported from Africa, South America, or Southeast and East Asia. The manner in which the central cavity of the spherulites forms, which when filled with cryptocrystalline quartz constitutes the thunderegg, is problematic and questions referring to the process by which cryptocrystalline quartz enters the central cavities of thundereggs encounter all the difficulties associated with understanding the formation of amygdaloidal agates.

The Geode Kid (aka Robert Paul Colburn), enjoying the advantages of having for 50 years mined thundereggs throughout the western United States, has advanced a developmental history of thundereggs in which, if there is a limited amount (0.1 to 0.2%) of wet or perlitic obsidian mixed in dry obsidian flows, it will be segregated and crystallize spherulitically into lithic flow bands. If the flowing stops or slows, yet remains at liquidus, the wet component can group into immiscible-like globules. At some temperature before the obsidian solidifies the globules will crystallize radially from the center out and form porous spherulites. If the external pressure is low enough, such as nearer the surface, the exsolved H₂O will coalesce into a cavity which then follows within the growing radial crystal aggregates forming stellate cavities. When these cavities are filled with agate or other cryptocrystalline quartz the spherulite is known as a thunderegg. Analyses of aphanitic shells sent by Colburn to the x-ray facility at the New Mexico Bureau of Geology and Mines showed 81.4% to 87% cristobalite. Back Scattered Electron images and quantitative chemical analyses showed 73.40% to 82.51% SiO₂. At the temperature of liquidus rhyolitic glass, the quartz polymorph would be H-cristobalite, which belongs to the isometric crystal system and has the common habit of forming spherical, fibrous aggregates, leading to the conclusion that H-cristobalite, not alkali feldspar, is the dominant former of spherulites.

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Chalcedony Occurrences in the Central Great Plains

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Introduction---Chalcedony is the most important gem mineral to be found in the central Great Plains both in terms of abundance, variety, and economic impact. The region contains chalcedony gems that have formed in place in marine sedimentary rocks, chalcedony gems that have been carried into the area by streams flowing eastward from the Front Range from the Oligocene to Recent, and chalcedony gems that have been carried southward from shield areas by glaciers of Pleistocene age. See Pabian (1971). These occurrences provide the collector with the opportunity to assemble a collection of both great variability and beauty, and provide a good guide to understanding some of the geologic processes that have been active in both the region and in source areas for these gems.

Chalcedony gems that have formed in place---Depending on whether you consider the Black Hills of South Dakota and the Hartville Uplift of Wyoming parts of the Great Plains, the agates that have formed in Pennsylvanian strata exposed here have been found in what appear to be shallow water marine limestone facies, and the silica source may have been volcanic ash or siliceous sponges. I personally favor the ash hypothesis even though volcanism was not important in the middle Pennsylvanian in the western interior, volcanism took place in other parts of the world. We have found some evidence of bentonites in the sedimentary record in the mid-continent, but such bentonites are not thick and obvious. These agates are commonly called Guernsey Lake agates in Wyoming, and Tepee Canyon agates in South Dakota, and were parent material for what are commonly called Fairburn Agates. Such agates have been found in Pennsylvanian strata as far away as eastern Nebraska, but they do not show the lively colors of the western material; in fact, they are rather ugly, but they are agates, and they represent similar sedimentary events in both places. Agatized chaetetids, sometimes called Sweetwater corals (Zeitner, 1957), also formed in Pennsylvanian of Wyoming, and these have been a popular chalcedony gem.

In south central Nebraska and north central Kansas, the Niobrara Chalk of late Cretaceous age has yielded colorful, bedded chert, much of which is olive green, but which may have streaks of red, yellow, and brown. These appear to be associated with bentonite suggesting volcanic ash as a silica source. It is interesting to note that none of this material contains shelly fossils, but some localities have yielded examples of this chert that contains shark teeth.

The Nebraska Blue agate has formed in place in wind blown deposits of siltstone and claystone in the Chadron Formation of Oligocene age in the northwestern panhandle, and similar deposits of agate have been observed in rocks of this age in South Dakota, where the small Black Hills Black agates have been found. The Chadron carries some examples of agatized wood, much of which is black. Some agatized nuts similar to walnuts and called *Juglans siouxensis* have been recovered from the Chadron in Nebraska.

Moss agate and moss opal have been recovered from the Ogallala Formation of Pliocene age in Nebraska, where moss opal was once commercially mined near Angora in Box Butte County. These deposits are extensive, having been found in neighboring South Dakota, northeastern Colorado, and in west central Kansas, when they were first described by Kunz as early as about 1885 (Kunz, 1885, Swineford and Franks, 1959).

Some of the pisolitic limestone described by Swineford, Leonard, and Frye (1958) that occurs in the Ogallala Formation, and is often associated with the moss agate and moss opal may be partially silicified and it resembles the Pennsylvanian chert of the Hartvilles and Black Hills, the parent material for Prairie agate, the Nebraska state rock. The pisolitic limestone and its Pennsylvanian counterpart are strong evidence for unconformities over large regions.

Some extensive deposits of agatized wood from the Ogallala Formation have also been observed in Nebraska and Kansas. The deposits along the Niobrara River near Valentine in Cherry County are very well known.

Chalcedony from western sources---Beginning in the Oligocene, the first large flood of clastic sediments derived from the erosion of the Front Range, Black Hills, and Hartville Uplifts reached the high plains of eastern Colorado, eastern Wyoming, and the western areas of Kansas, Nebraska, and the Dakotas. Perhaps the most famous gem to be found in these deposits is the Fairburn agate, a stone named for Fairburn, South Dakota. There appear to be multiple sources for the Fairburn agate, including the Front Range, the Hartvilles, and the Black Hills. In Wyoming, many of these agates were collected near Shawnee, and they were simply called fortification agates, without reference to the town of Fairburn. Some of the Fairburn agates may have actually been eroded from their source in the late Cretaceous and deposited in conglomerates of the Dakota Group, but none of these strayed far from the Black Hills. See Connolly and Oharra (1929). These agates have been found in stream deposits of both Pleistocene and Recent ages in South Dakota and Nebraska, where they may have been eroded directly from the Pennsylvanian parent material or eroded from younger agate bearing gravel of Oligocene age.

Jasper from western sources is abundant throughout any of the gravel deposits of Oligocene age in Wyoming, South Dakota, and Nebraska. The jasper had multiple sources, and some examples have fossils of Ordovician age and Devonian age, as well as some having fossils of Pennsylvanian and Permian age. These jaspers are commonly referred to as Prairie agate, although none is spherulitically crystallized as are the tightly banded Fairburn or fortification agates. It is interesting to note that the Tertiary gravels of Miocene and Pliocene ages usually carry no examples of the above agates or jaspers. Most of these gravel deposits consist solely of large cobbles of continental limestone, and they are commonly called class "D" gravel.

The North Platte River in Nebraska carries some fine examples of agate, jasper, and agatized wood, most of which appears to be from Hartville and Front Range sources. There are examples of banded agates that are similar to Fairburns, and these may be found as far east as Cass and Sarpy counties, bordering the Missouri River.

The South Platte River gravel, both in streams and terraces, has been my personal favorite for collecting chalcedony gems. Banded agates are rare here, but the gravel deposits in Deuel County have yielded some fine examples of moss, dendritic, and plume agates. Agatized wood of many fine colors and patterns, and coming from Cretaceous sources in Colorado, are plentiful in Deuel County and the South Platte River. Much of the wood appears to be from

coniferous trees but some hardwoods, cycads, and palm fragments have been found. South Platte River jaspers are numerous in color and variety, and a whole treatise could be devoted to these alone.

The Republican River of Nebraska and Colorado has produced examples of agatized wood and some fine examples of dendritic agates that may be eroded from the moss agate deposits of the Ogallala Formation. Gravel of the Smoky River of Kansas has yielded some examples of agatized wood and some scarce banded agates.

Each drainage basin in the study area contains an almost unique suite of chalcedony gems, suggesting that each stream drained a different area of the Front Range.

Chalcedony in Glacial Deposits---Glacial deposits in the central Great Plains extend through eastern South Dakota and along a line that is approximately parallel to and about 70 miles west of the course of the Missouri River in Nebraska, and into northeastern Kansas. The glacial deposits in northeastern Kansas have yielded some extremely fine and large examples of agates that have been called Lake Superior agates because of their similarity to material from Minnesota and Wisconsin. Whether or not all of these agates came from the late Precambrian Keweenaw Basalts is a moot question. Probably many of them did, but some may have formed in younger sedimentary rocks in northern sources, but no such sedimentary agate sources are currently known. These agates have been found in glacial tills in southeastern South Dakota and much of eastern Nebraska. Some of these agates have been found in outwash from glacial till as far west as Kearney, Nebraska, but they are not common in these post-glacial deposits. It is of note that in Minnesota, Lake Superior agates are most commonly found in tills of Wisconsin age, about 12 thousand years before present (ybp). Boellstorff (1978) has dated volcanic ashes in the Pleistocene of Nebraska and Iowa, and ash dates that are associated with one of the prolific agate bearing units in Nebraska are about 230 thousand ybp.

Because the glaciers scoured through an extensive geologic section that extended from the middle Precambrian through almost the entire Paleozoic, and over a large geographic area, there are many kinds of gem chalcedonies to be found in the extensive till deposits. Agatized coral and stromatoporoids that are of Devonian age may have originated in the Lake Winnipeg area of Canada, whereas the agates most likely originated in the Keweenaw basalts of Minnesota and adjacent Ontario. There are numerous examples of very colorful jasper that have been found in the glacial deposits of the Dakotas, Nebraska, and Kansas. Glacial tills here have yielded some agatized wood, but most is of poor quality, and in small pieces, and this probably reflects the lack of forests in the Paleozoic of the source areas.

Conclusions---Combined with the chalcedony gems that have formed in place in the central Great Plains, the multiplicity of lithologies in western and northern source areas have provided a great assortment of chalcedony gems, and they provide many clues to understanding the geology of this area.

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Australian Agates and Thunder Eggs: Why One is Never Enough

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Australia is the Lucky Country when it comes to agate and thunder eggs, for variety, colour, size, texture and number of collecting localities in this huge continent. We even name our most famous collecting area Agate Creek. Connoisseurs of Australian agates and thunder eggs can recognise the locations from the specimens because of their distinctive identification qualities. This talk will focus on the variety of agate and thunder eggs found “Down Under”, their geological setting, the methods of collecting and what makes fossicking for Australian agates and thunder eggs unique.



This huge cut and polished agate, which is 24 inches across, displays some of the range of colours of the Agate Creek agates.

Both agates and thunder eggs are associated with volcanic rocks with the rule of thumb being that agates are found in basaltic rocks and thunder eggs in rhyolitic rocks. Although Australia is an old continent with no current volcanism, many volcanic rocks from past eruptions are currently exposed and agates and thunder eggs may be found in the same general vicinity in areas of multiple volcanic episodes. The age of the host rocks varies from Cambrian to Tertiary and some, but not all, of these volcanic rocks contain agates and thunder eggs.



Australian thunder eggs on display at the University of Wollongong

The Khur Agate Field, Central Iran

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Abstract

The agates of Khur, Central Iran are described together with the local topography, climate and geology of the Khur region. The agates have been examined using SEM with EDS and XRD techniques. It is proposed that the source of the silica for the agates is the prolonged hydrothermal activity in the area during the Eocene Epoch. The detection of evaporitic minerals suggests that a saline regime of ground water was, at least in part, a secondary process in the genesis of the Khur agates.

Introduction

Agates are found throughout the world as silica deposits within gaseous cavities of some volcanic rocks. In the ancient world, Iran had a reputation as a source of good quality agates. These were to be found in several extensive volcanic provinces that extend over vast districts in this country. In prehistoric times, agate was valued among Iranian clans as a semi-precious mineral and a talisman. These early Iranians revered agate geodes as a wonderful stone that had magical powers and named them "Devil's eggs" (Zavush, 1996).

Unfortunately, there are no historical records about the mining of Persian agate. It is likely that the first collectors obtained their samples directly from the desert surface. This tradition continues and today's collectors follow the old methods and continue to collect surface material. There has never been mechanical digging of Iranian agate. Collection has always been restricted to the surface nodules or hand digging in shallow pits. The most celebrated Iranian agate localities are located in the central and eastern parts of Iran. Interest in agate is limited to the few amateur and professional collectors who continually seek new sites.

The Khur agates have long been celebrated for their fine blue banding and this paper is the first scientific study on the agates and their associated minerals. The sole brief account of agates and geodes of Khur is in an explanatory text of the metallogenic map (1:250,000) of the Anarak area (Romanko et al., 1984).

Topography and climate of Khur

Khur is a typical mountain desert area lying in Central Iran between Tehran and Yazd. It includes several isolated and varied mountainous massifs with elevations from 1000-2450 m. This area also includes the southern periphery of the Great Kavir Depression. Inter-mountain basins are occupied by gently tilting sand and pebble plains (Dasht) that pass into salt flats. Locally developed eolian sands are to be found in the central part of the basins.

The Khur climate is extremely arid with daily temperatures in July-August rising to 45 °C in the shade and dropping down to -15 °C in January. Rain, together with snow, is in the winter but the annual precipitation is only about 50 mm. Winds during winter and spring frequently

give rise to ferocious sand storms. These extreme conditions mean that autumn (October-November) and early spring (February-March) are the most favorable seasons for fieldwork. The Rudkhaneh-ye-shur is the only perennial river in the area; this runs some 5-6 km north and northwest of Khur that rises out of brine springs in foothills. Valleys can become temporary watercourses for the melting snow. The abundant short showers cause mountainous mudflows while low discharging springs can be found locally at the foot of the mountains. Non-potable, highly mineralized spring water is obtained from underground artificial channels (named Qanat).

Khur city, with a population of 7500, is the largest habitation in the area. Minor settlements in Chupanan, Chah Malek, Farrokhi and Mehrjan can be found along the Anarak-Khur-Yazd automobile road.

The Khur agate locality (55° 17' E, 33° 39'N) is approximately 25 km southeast of the Khur city and the nearby Kavir bentonite mine is the only active mine in the area. Access to the Khur agate fields is from the Khur-Tabas automobile road turning onto a dirt road which passes from Tashtab oasis via the Kavir bentonite open pit mine (Fig. 1).

Geology of the Khur district

The Khur area is composed of different rocks ranging in age from Proterozoic to Cenozoic. The most prominent structural feature in the area is composed of Upper Proterozoic-Paleozoic metamorphic rocks with an overlying cover of mostly Cretaceous and Paleocene rocks.

Volcanic and sedimentary rocks, deposited between 53 and 48 Ma ago, form an important part of the geological sequence of the area. Volcanic rocks lie unconformable on subjacent rocks of different ages and overlain transgressively by continental sedimentary rocks of the Pis Kuh Formation. In most areas, the volcanic sequences are about 600 m thick. The rocks are formed in the order: tuffaceous andesite, andesite-dacite and dacite. As a general rule, only the basal tuffaceous unit hosts agate and geode bearing layers (E1 in Fig. 2). This unit varies in thickness from 30 to 200 m, but is about 100 m thick in the locality of the agate amygdales on the northwestern slope of Howz-e-Mirza Mountain. The tuffaceous conglomerate which grades upward to a thin interbedding of brick red, pink, gray inequigranular tuffstone. These are individual and non-persistent vesicular flows of dacite and andesite lavas among tufa layers. In some places, agate and geode nodules are formed in these gas vesicles.

Unweathered parts of the lava flows sometimes contain nodules near to the associated network of fissures. Such fissures could act as conduits for late volcanic hydrothermal fluids. Undoubtedly these fluids are responsible for the partial bentonitization within the tuffaceous unit (Fig. 3). Associated flows of pyroclasts consisting of fragments of andesine, amphibole, quartz, and biotite cemented by ash material are also to be found within the tuffaceous unit. The low angle of dip of the Eocene volcanic sequences means that this tuffaceous basal unit has few obvious outcrops in the south and southeast of Khur (Aistov et al. 1984).

In some outcrops, this unit has been metasomatically altered into bentonite. Formation of these montmorillonite deposits is associated with late hydrothermal activities (Romanko et al., 1984). A group of such deposits is located southeast of Khur which coincides with the deposition of agates and geodes. Kavir Mine, the largest deposit of bentonite in the area, is being exploited by the petroleum industry. Here, the tuffaceous mother rock contains interlayers of andesite lava flows with amygdales together with gravelstone, conglomerate cemented by ash and calcium carbonate.

A lack of any deep excavation within the bentonite mine prevents any detailed knowledge about the spatial distribution of agate inside the tuff layer. Surface nodules do not have any regular distribution and are often found as scattering distinct clusters. This suggests that the agates were originally formed in groups and intense weathering resulted in these surface clusters (Fig. 4).

Khur agates

The Khur agate field is cut by several large normal faults that occurred after the Tertiary Period. The fault strikes are mostly NE-SW to E-W and are several kilometres in length. Many agates show evidence of faulting. Single nodules have been fractured and then were re-joined by a later cementation by secondary chalcedony and jasper (Fig. 5). Similar structural features have been recorded from the other agate fields throughout the world (Cross, 1996). The nodules themselves are mostly ellipsoid to almond in shape but some spherical and irregular nodules can be found. All agates have a rough external surface that is yellow brown to dark gray in colour and composed of a mixture of calcite, limonite, siderite and clay minerals. This outer crust is generally about 1 to 3 mm thickness, but exceptionally it can be up to 50% of the total volume (Fig. 6). Fresh nodules are covered with a thin green crust of celadonite.

A detailed study of 827 agate amygdals shows:

- The diameter of nodules can vary between 10 to 180 mm. More typically, the diameters are in the 45 to 50 mm range. About a quarter of nodules would be classed as commercial quality. Banded agate, without central quartz filling, forms less than 4% of whole nodules.
- Many of the Khur nodules are composed of agate layers with a central region which is fully or partially filled with colourless crystals of quartz. The macrocrystalline quartz in nodules can occupy up to 50% of total interior volume.
- Khur agates have a limited range of colour. They are mostly pale to inky blue but some of them are grey, white, colorless and more rarely red. A red colouration is restricted to some of the chalcedony bands of smaller nodules or along internal fracture cracks of larger ones. Mineral inclusions of aragonite and goethite are common. Such inclusions can be found in all the agate types: moss, plume, flame, eye and fortification agate (Figs. 7 to Fig. 11).
- Geodes with hollow centers formed less than 7% of all the nodules. The interior wall of Khur geodes is mostly lined with colourless, euhedral quartz crystals (Fig. 12). Some of the geodes exhibit fine crystals of amethyst. These amethyst crystals are universally pale violet in colour (Fig. 21). In addition, some pale green quartz crystals have been recorded (Fig. 13). It has been suggested that the green colour is due to the secondary heating of primary amethyst (Webster, 1983 & O'Donoghue, 1987).

Analytical Methods

A number of minerals have been identified either visually, microscopically, using X-ray diffraction (XRD) scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

X-ray diffraction

The samples powder was ground to under 200 micrometer size. The powder was examined in SEIFERT T2T 3000 X-ray diffractometer with Cu tube, 30mA, and 40kV in the range of 2 theta from 5° to 60° at a scan step of 5° 2-theta/min.

Scanning electron microscopy

A standard SEM technique used to examine freshly fractured agate samples and mineral inclusions being coated with gold and examined at 5 KV in a Phillips XL30.

Energy dispersive spectroscopy

The above SEM apparatus equipped with an EDAX DX41 energy dispersive X-ray spectrometry system that used for analyzing the small quantities of microminerals where there was insufficient for identification by XRD. The EDS could not entirely identify a mineral. Thus this analytical method used along with other visually and microscopically specifications to determine the outside chemical formula for observed minerals.

Minerals

Khur agates have been observed with a totally different mineralogy from their immediate neighbors. This would support the suggestion that identical starting conditions still produce unique agates (Macpherson, 1989). The following twelve minerals have been identified from the agate and geode samples found in the Khur agate fields. The minerals can be divided as essential and secondary. Essential minerals are composed of chalcedony and quartz. Accessory minerals are generally alteration products of the host rock and could be placed in three suites according to their genetic formation. Pre-banding deposits occurred before the crystallization of the silica gel; syn-banding inclusions which formed contemporaneously with the chalcedony or quartz crystals. Post-banding minerals formed after the agate bands (Pabian & Zarins, 1994).

Chalcedony SiO₂

Cryptocrystalline quartz or chalcedony is the single most abundant mineral both in agate and geode nodules at this locality. Rhythmic, wall-lining chalcedony is the sole form of this mineral in agate nodules (Fig. 11) and no sample with horizontal banded layers has been recorded in this region.

As a general rule, the intensity of colour and the thickness in the chalcedony banding is less pronounced when compared with similar agates from other localities. SEM studies of chalcedony bands in the Khur agates showed that the clear chalcedony is more globular than fibrous. This globularity has been shown in banded agates from other regions (Moxon, 2002). The extensive presence of quartz grains with a near equal size to chalcedony bands is another reason for weak appearance of bands in Khur agates (Figs. 14 & 15).

Occasionally, some of the well-known varieties of agate can be seen among sections of Khur agates.

- Plume agate was observed when filaments of a golden-brown feather-like goethite and siderite rested in a matrix of colorless to blue translucent chalcedony (Fig. 8). Moss agate, resembling moss and similar growth of plant life, was produced when fine inclusions of calcite had been covered with black manganese dioxide. In some cases, irregular patterns have been embedded in silica layers (Fig. 7).
- Sagenite agate can be seen when fan like clusters or “sprays” of yellow to white embedded needles of aragonite crystals. (Fig. 16).
- Flame agate is shown by “tongues” of pale blue flame-like banding structures (Fig. 9).
- Pompon agate in which yellowish aragonite inclusions are arranged in patterns resembling pompons.
- Fractured agate in which solutions have penetrated and dyed a portion of agate (Fig. 18).
- Stalactite and botryoidal aggregates of clear to white chalcedony are occasionally found. These are always found as an interior lining and resemble the Palomas geodes from Mexico (Cross, 1996).

Quartz SiO₂

Macroquartz is very abundant as crystals in geodes and in the centers of some agates (Fig. 12). Crystals up to 20 mm have been observed. The quartz is typically euhedral and is usually colourless (rock crystal). Amethyst occurs as pale purple lustrous crystals to 10 mm (Fig. 21). In some cases, a colour sequence of colourless quartz to pale-violet amethyst is observed.

Calcite CaCO₃

Calcite is the most abundant secondary mineral. Calcite can show a wide variety of forms and sizes within Khur nodules. This mineral may be found as a pre- (Fig. 22) or a post-banding inclusion (Fig. 23), or as a pseudomorph after other minerals. Also it can be partly or fully replaced by quartz or chalcedony.

Calcite can range from colourless to pale-yellow crystals in a variety of crystal forms. These include both coarse scalenohedral and rhombohedral crystals. The surfaces of some calcite crystals were incrustated with a smoky film of Mn-Fe oxide minerals. In most cases calcite can be found as a pseudomorph after aragonite or as dendritic aggregates of Mn-minerals (Figs. 24 & Fig. 25). Scalenohedral forms of calcite are more abundant than rhombohedral crystals (Fig. 17). The calcite crystals may reach 30 mm in length. Snowball agates show a complex aggregate of an intergrowth of calcite and quartz (Fig. 27).

Aragonite CaCO₃

Aragonite occurs mostly as syn-banding, orthorhombic needle-like inclusions within chalcedony layers and forming “sagenite agate” (Fig. 16). In a few agate nodules, pseudo-hexagonal crystals of aragonite have been completely replaced with quartz and chalcedony (Fig. 28). Aragonite was identified by an XRD examination of its powder and by studying the forms and surfaces of its crystals.

In some agates, needle-like crystals of aragonite were arranged as a fine compact divergent aggregate around a nucleus near the wall of the vesicle. The crystals formed a hemisphere structure that was later covered with chalcedony layers as a pre-banding inclusion, and formed “pompon agate”. In most of the above cases, calcite may be regarded as a pseudomorph after aragonite.

Pabian (1978) and Keller (1977) proposed that the presence of low-temperature deposits of aragonite and gypsum, as protogenetic inclusions, might show that the agate hosts were formed at a low temperature (25-30°C) and at low pressure.

Dolomite (Ca,Mg)(CO₃)₂

Dolomite is a relatively rare mineral in Khur nodules and generally cannot be distinguished from other carbonate minerals with the unaided eye. This mineral was identified by an XRD examination of a snowball agate. Dolomite generally found as a white to yellowish, compact to spherulitic fibrous masses, which intergrow with quartz crystals. This assemblage could fill some of the vesicles completely and form a snowball (Fig. 27).

Siderite FeCO₃

Siderite is a common mineral in Khur agates. This mineral with its yellowish brown color is not only one of the crust-forming minerals, but it can be seen as a dye that produced individual colorful bands with colloform texture. In some instances, attractive plume-like pre-banding inclusions were observed in the chalcedony bands (Figs. 6, 8, 26, 29). Fine brown rhombohedral crystals of siderite have been seen with calcite, as overgrowths on macroquartz crystals (Fig. 30). Siderite was identified by an XRD examination of its powder.

Anhydrite CaSO₄

Anhydrite has only been observed as a remnant mineral on the microscopic scale in the snowball agates. These agates are a rare type among the Khur nodules. Nodules are filled with a milky mixture of quartz, calcite and other uncommon minerals such as dolomite and goethite (Fig. 26 & Fig. 27). Some structural types appear as hollows after primary minerals have been leached. Other samples show features which have been completely replaced by quartz and calcite. These structures can be seen with the unaided eye.

A few thin sections show a remnant mineral beside quartz that have a moderate relief with birefringence and parallel extinction. The outer line of this remnant mineral is commonly castellated through right-angle re-entrants, indicating 90° cleavage (Fig. 37). The optical characteristics show that these remnant mineral crystals are composed of anhydrite. However we have not seen anhydrite-filled geodes during our studies. The “snowballs” were initially nodules filled with anhydrite crystals. Later, the anhydrite has been replaced more or less completely with quartz and calcite.

Goethite FeO(OH)

Goethite and its earthy aggregate limonite is a common mineral both in agates and geodes of the Khur area. Limonite, with its feather-like appearance, is generally seen as a crust-forming mineral, but exceptionally may be seen as a yellow pigment in chalcedony bands. This mineral is frequently found with siderite. Goethite can produce pre-banding, needle-like crystals up to 3 mm that are reddish-brown to black (Fig. 31). Goethite inclusions have been observed as overgrowths on the surface of quartz crystals. The SEM micrographs show divergent sprays of goethite composed of either feather-like or individual flat needle-like crystals and EDS identified the goethite crystals (Figs. 32, 33).

Pyrolusite MnO₂

Pyrolusite is a common inclusion in Khur agate nodules. This mineral is either observed as dendrites within individual bands (Fig. 25) or as irregular masses, which appear to float in chalcedony layers (Fig. 18). Pyrolusite is commonly associated with calcite crystals and overlays them as a smoky thin layer. In most of the dendrites, calcite has partially replaced the pyrolusite. Pyrolusite was identified by an XRD examination of its powder.

Hematite Fe₂O₃

Hematite is rarely found in the Khur agates. This mineral, when observed, occurs as discontinuous red layers scattered as a pre-banding inclusion. In a few agate samples, hematite filled some parts of secondary interior cracks and dyed them red (Figs. 18, 34). Hematite was identified by an XRD examination of its powder.

Celadonite KFe³⁺(Mg,Fe²⁺,Al)Si₄O₁₀(OH)₂

Celadonite occurs very rarely as a thin dark green crust on the outside of the nodules still embedded in their host rock (Fig. 3). Celadonite has not been observed on loose nodules and the mineral has probably been removed by weathering. Because of some restriction in analysing clay minerals by XRD, this was visually identified by its color.

Celestite SrSO₄

Celestite has been recorded on a few quartz-lined geodes as a colourless to pale blue short orthorhombic prisms with divergent column aggregates. This mineral was revealed during EDS studies on the geode's contents; the crystal sizes reach to over 15 mm in length and they are often accompanied by calcite crystals (Fig. 35). Celestite was identified by its strong peaks of Sr and S in EDS examination on one of the individual crystals, and also by its crystallographic characteristics.

Chrysocolla (Cu²⁺,Al)₂H₂Si₂O₅(OH)₄.nH₂O

Chrysocolla is a very rare mineral in Khur nodules. This mineral is found as a fracture filling in a unique agate sample (Fig. 36). Chrysocolla was identified by its optical characteristics in thin section.

Auricalcite (Zn,Cu)₅(CO₃)₂(OH)₆

Auricalcite divergent sprays of about less than 0.5 mm length were observed as overgrowths beside calcite crystals on the surface of quartz crystals in only 2 geode samples. The binocular photomicrograph (Fig. 38) shows divergent sprays of auricalcite composed of light blue needle-like crystals. EDS results in addition to crystal habit suggested the auricalcite formula for this mineral.

Discussion

It is not intended to discuss in detail the process of agate formation as the problems of agate genesis have been discussed by many authors Landmesser (1984), Pabian & Zarins (1994) and Moxon (1996) and the literature therein. This discussion will focus on the relationship between the genesis of agate and post volcanic hydrothermal processes that resulted in the bentonitization.

It seems that low to medium temperature ascendant hydrothermal fluids have altered the primary composition of volcanic tuffs. These volcanic tuffs show remnants of hydrothermal conduits which extensive distribution of secondary minerals especially clay and silica accompanied them (Fig. 38). Solutions of silica and metallic cations would migrate from altered tuffs and form agates, geodes and secondary deposits in any suitable gas vesicles and vein. It is believed that hydrothermal activity due to long-lasting volcanic occurrences in the Eocene and in the Khur area (Stocklin, 1968) is sufficient to supply the necessary silica for the agates. It is proposed that the associated assemblage of well-formed crystals of secondary minerals is evidence for the formation of a low temperature (<100 °C) agate formation. However the presence of some evaporate minerals e.g., anhydrite and gypsum, bring out the chance that a saline regime of ground water has affected the mineralogy of, at least in part, geodes as a secondary process.

It has been well documented that the solidification of lava will trap gas bubbles (Macpherson, 1989). It is usual for the majority of vesicles (and therefore the amygdales) to be concentrated at or near the upper margin of an individual lava flow as a result of the upward escape of gases from within the lava. Unfortunately, the low dip of the tuffaceous units, its interlayer lava flows and the absence of any deep exploration prevents any comment on the frequency of amygdale occurrence in these host rocks.

Other agate bearing assemblages of similar tuff and interlayer vesicular lava flows have been recorded from the agate fields of Northern Mexico (Cross, 1996) and the Cathedral Mountains of West Texas (Zarins, 1977).

Conclusion

In all probability, the tuffaceous unit and its associated lava andesitic interlayers have all erupted and been deposited in a shallow continental basin. A continental margin and subduction zone occurred in Central Iran during the Eocene (Berberian & King, 1981). Extensive volcanic fields, associated with these Continental margins and subduction zones have been recorded as one of the important tectonic settings of nodular agate occurrences (Pabian & Zarins, 1994).

Post volcanic hydrothermal alteration resulted in the formation of bentonite. This must have started after the deposition of the volcanic sequences but before the beginning of the diagenetic processes. Mineralogical and textural evidence indicates that the agates and geodes have been formed under low temperature conditions. It is likely that the desilicification of bentonite forming reactions could be one possible silica source for the formation of the Khur agates and geodes. Such a close relationship between agate and bentonite formation should be considered as one possible mechanism for agate and geode genesis.

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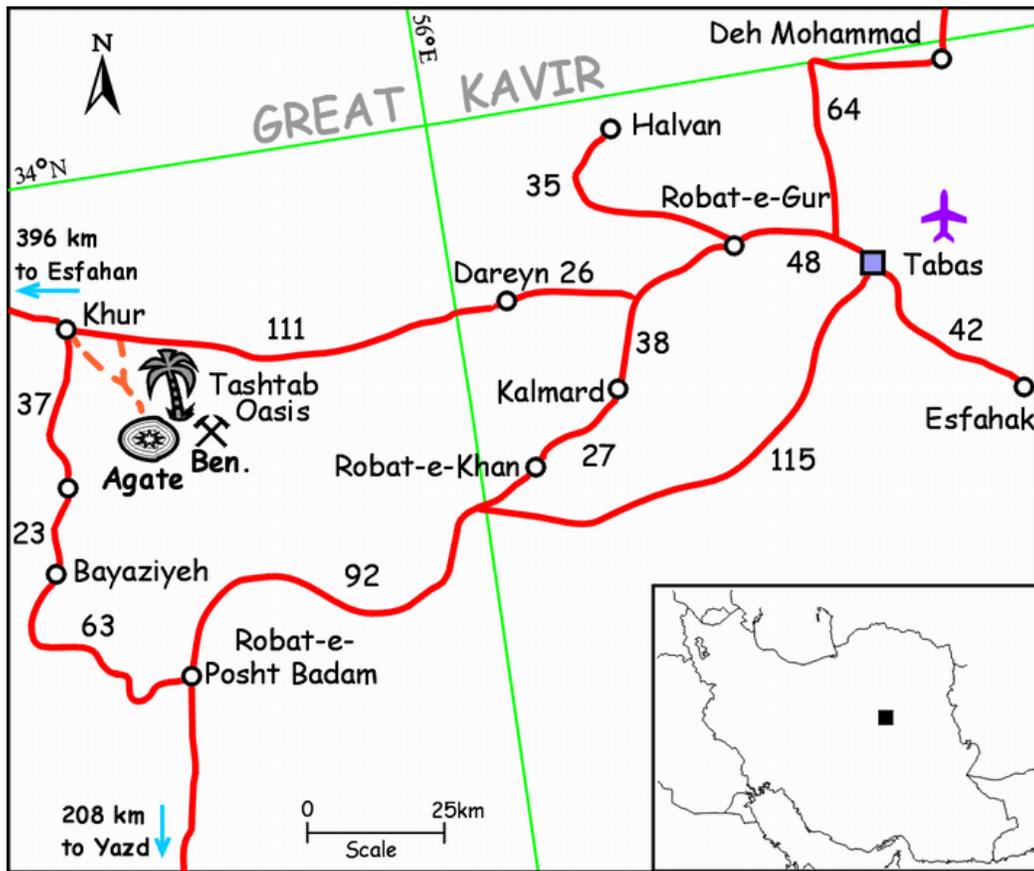


Fig.1 The route map of Khur area.

L E G E N D

QUATERNARY		<p>Q^{4p} - Proluvial pebble gravel, clayey sand. Q⁴ⁱ - Takyr (clay flat): clayey sand. Kavir. Q^{4s} - Salinized clayey sand. Q^{4k} - Salinized sandy clay. Q^{4e} - Clayey salt. Q^{4l} - Lake clay. Q^{4e} - Eolian sand</p>	
		<p>Q^{3ap} - Low dash: alluvial-proluvial pebble gravel, sand, conglomerate. Q^{3l} - Lake sand and clay</p>	
		<p>Q^{2ap} - Middle dash: alluvial-proluvial pebble gravel, sand, conglomerate. Q^{2l} - Lake sand and clay</p>	
		<p>High dash: alluvial-proluvial pebble gravel and sand (often with gypsum), conglomerate, gravelly sandstone</p>	
PLIOCENE	Pl	Conglomerate, pebble gravel, sandy clay	
MIOCENE	M _r	Upper red formation. Clay, often sandy, in places gypsinate; sandstone	
OLIGOCENE	OM _a	QOM FORMATION. Clay, limestone, sandstone, conglomerate	
LOWER EOCENE	E ₁ ⁱ	Andesite, dacite and their tuffs, basalt	
	E ₁ ^j	Tuff, tuffaceous sandstone, dacite, andesite; basal tuffaceous conglomerate	
	E _d	Grey conglomerate, sandstone, marl	
	E _d ⁱ	Red sandstone, conglomerate, mudstone, marl, limestone	
PALEOCENE	Pe _{ch}	Chūpānān formation. Pelagic limestone	
CRETACEOUS	DANIAN	K ₁	Limestone (often with chert), marl, sandstone
		K ₁ ^u	Marl, limestone
	UPPER SENONIAN	K ₂	Marl, limestone } Farrokhi formation
		K ₂ ^u	Haftoman formation Limestone with rudists, sandy, in places argillaceous limestone, gravelstone
	CENOMANIAN	K ₃	Marl, limestone
		K ₃ ^u	Organic- detrital limestone, sandy limestone, sandstone, gravelstone
	TURONIAN	K ₄	Bāzyāb formation. Green-grey marl, argillite, limestone, occasionally sandy
		K ₄ ^u	Interstratification of shale, siltstone, limestone, sandstone
	ALBIAN	K ₅	Shale, limestone; calcirudite and conglomerate at the base } Mirzā formation
		K ₅ ^u	Marly slate, clay slate, limestone, occasionally sandy
APTIAN	K ₆	Clay slate, slaty mud shale, marlstone, limestone } Biābānak formation	
NEOCOMIAN	K ₇	Shah Kūh formation. Orbitolina limestone	
JURASSIC	JK ₈	Noqrēh formation. Sandstone, marl, limestone, conglomerate	
	JK ₉	Chāh Palang formation. Mud shale, sandstone	

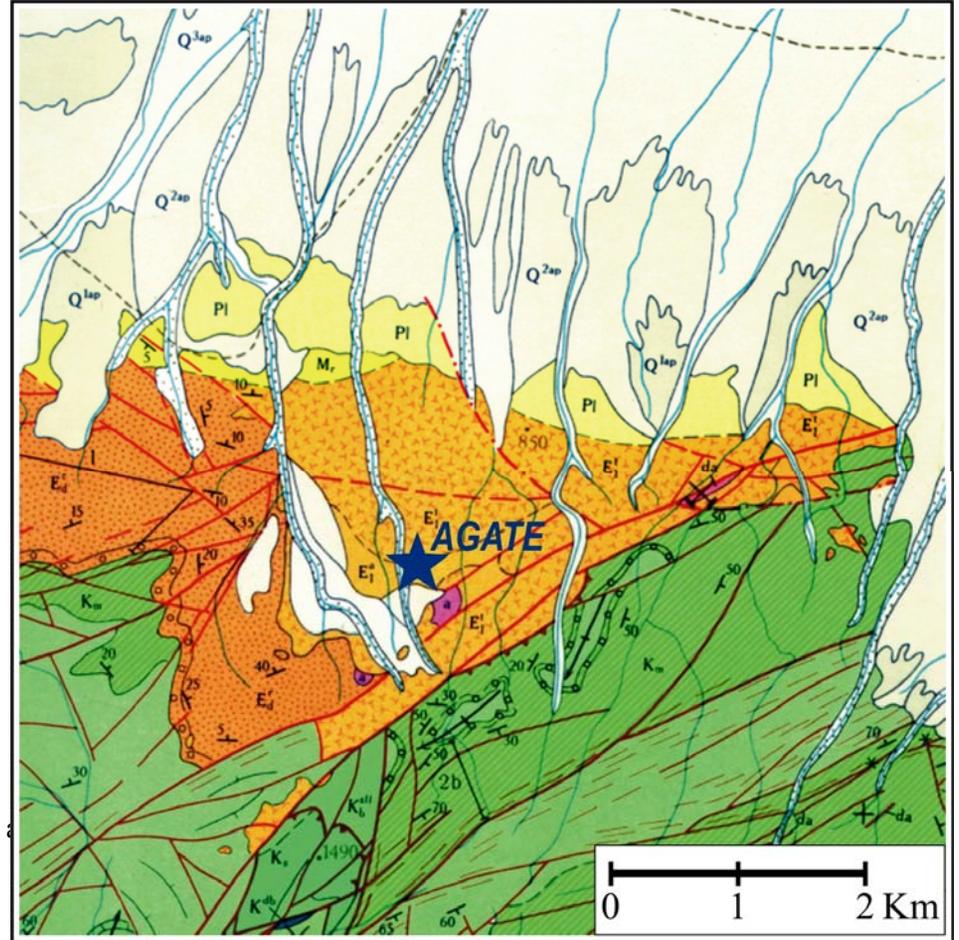




Figure 3. An agate nodule with its green celadonite crust and hydrothermal fissures in the andesitic host rock. Specimen measures 43x38 mm.



Figure 4. Scattered loose nodules on the surface of the earth.



Figure 5. An agate nodule which has been offset due to regional faulting. The fractions were re-joined by a later cementation. Specimen measures 66x32 mm.



Figure 6. An agate nodule with a very thick limonite crust. Specimen measures 51x45 mm.

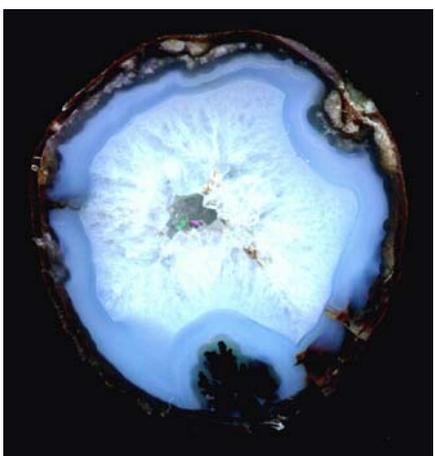


Figure 7. Moss agate. Specimen measures 41x38 mm.



Figure 8. Plume agate. Specimen measures 63x55 mm.



Figure 9. Flame agate. Specimen measures 47x36 mm.



Figure 10. Eye agate. Side edge represents 24 mm.

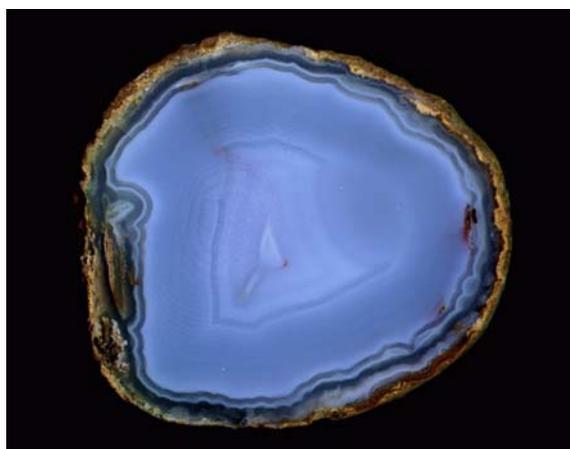


Figure 11. Fortification agate. Specimen measures 58x53 mm.

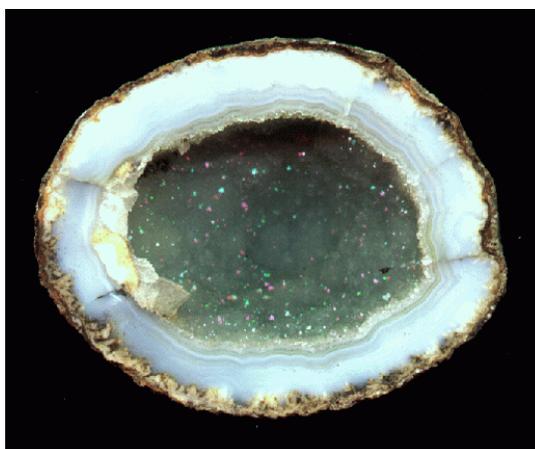


Figure 12. Quartz geode. Specimen measures 52x42 mm.



Figure 13. Green quartz with tube of escape structure. Specimen measures 94x76 mm.

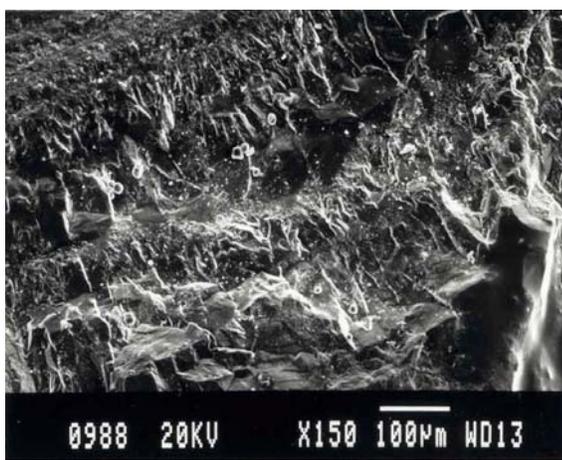


Figure 14. An SEM micrograph showing microcrystalline quartz in the foreground with weak alternating white banding and clear chalcedony in the upper left hand corner in the fractured surface of an agate from Khur, Iran (photo T.J. Moxon).

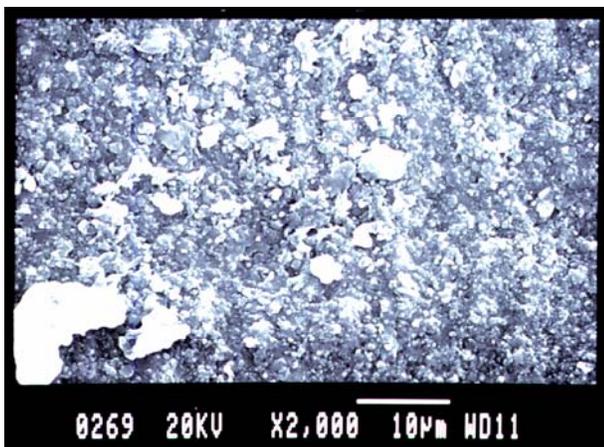


Figure 15. SEM photo of the fractured surface of weak banding in agates from Khur, Iran (photo T.J.Moxon).



Figure 16. Saginite agate. Side edge represents 11 mm.



Figure 17. Growth of scalenohedral calcite on quartz crystals in a geode. Side edge represents 6 mm.

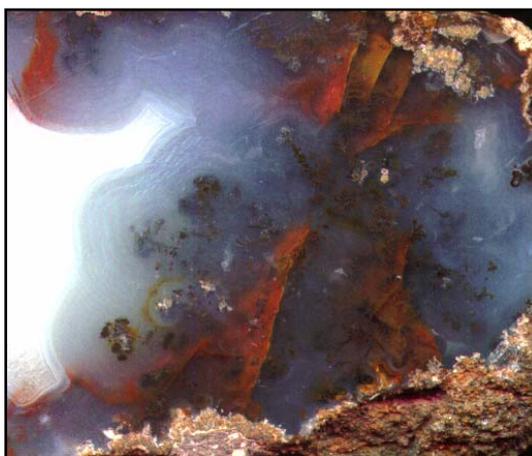


Figure 18. Fractured agate with floating dendrites. Fractures filled with secondary pigments of hematite. Side edge represents 34 mm.

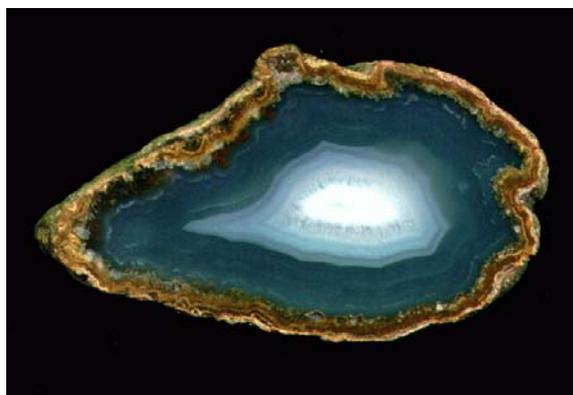


Figure 19. Inky blue agate. Specimen measures 52x32 mm.

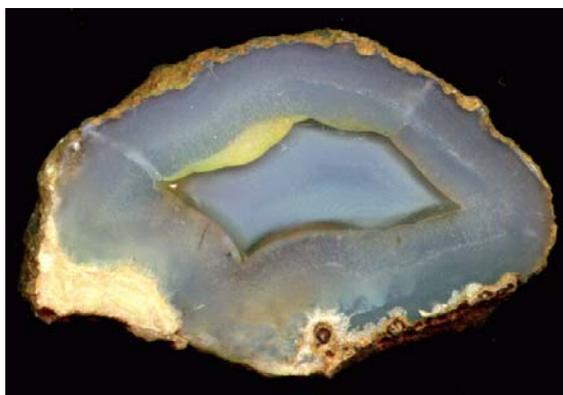


Figure 20. Gray color agate. Specimen measures 57x37 mm.



Figure 21. Geode with a lining of pale violet amethyst crystals. Specimen measures 24x15 mm.



Figure 22. Pre-banding inclusions of calcite crystals. Side edge represents 20 mm.



Figure 23. Post-banding inclusions of calcite crystals. Side edge represents 8 mm.



Figure 24. Aragonite bands replaced with Mn minerals. Specimen measures 43x36 mm.



Figure 25. Dendrites of pyrolusite replaced with calcite. Side edge represents 23 mm.



Figure 26. Spherulitic growth of siderite bands in a snow ball composed of calcite and quartz. Side edge represents 18 mm.



Figure 27. A snow ball composed of dolomite and quartz. Specimen measures 36x33 mm.



Figure 28. Pseudo-hexagonal crystals of aragonite replaced with chalcedony and quartz. Side edge represents 31 mm.



Figure 29. Brown pigments of siderite in chalcedony bands. Specimen measures 39x31 mm.



Figure 30. Growth of siderite rhomboherdral crystals in a geode. Side edge represents 4 mm.

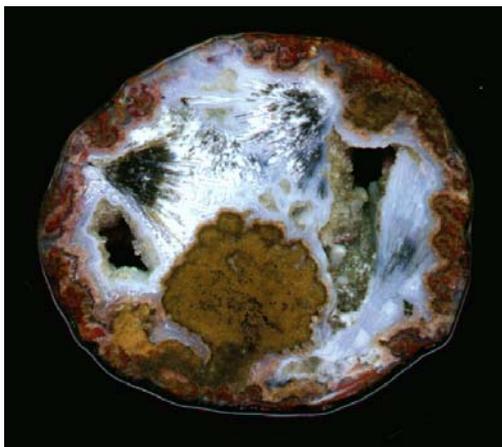


Figure 31. Pre-banding needle-like crystals of goethite in an agate. Specimen measures 39x34 mm.

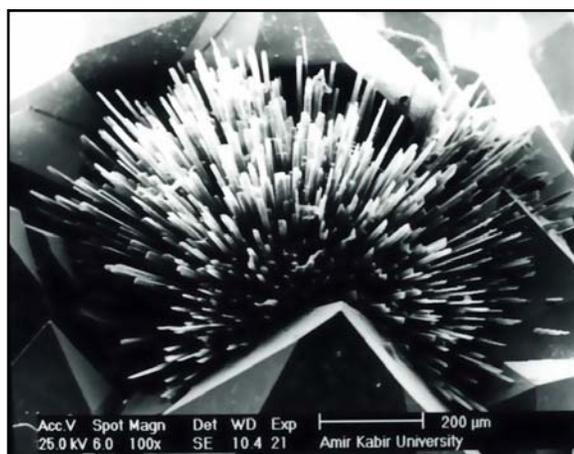


Figure 32. SEM image of flat needles of goethite on quartz crystals in a geode.

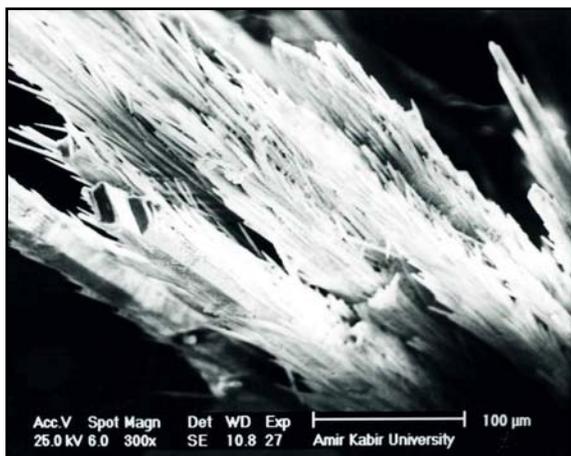


Figure 33. SEM image of goethite crystals with feather-like aggregate.



Figure 34. Agate nodule with red bands. Specimen measures 31x25 mm.



Figure 35. Celestite crystal growth in geode. Side edge represents 8 mm.

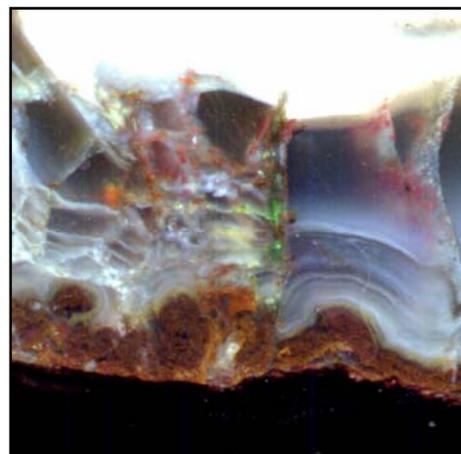


Figure 36. A crack in agate bands, which filled with chrysocolla. Side edge represents 21 mm.

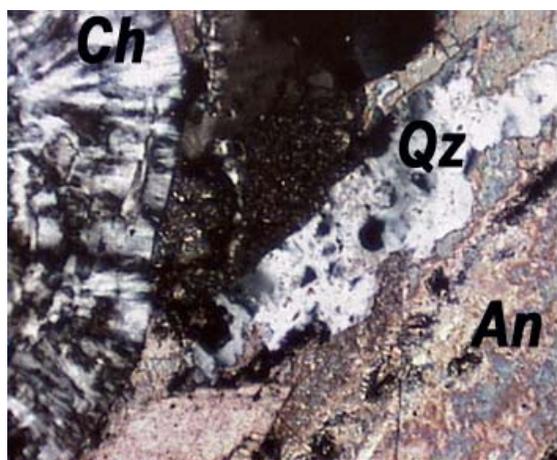


Figure 37. Anhydrite remnant (An) between quartz(Qz) and chalcedony bands(Ch). Thin section of a snow ball agate (polars crossed 40x). Side edge represents 0.8 mm.



Figure 38. Growth of blue auricalcite crystals with coloform aggregate around the base of a celestite crystal, on quartz lining of a geode. Side edge represents 4 mm.

Fluid Inclusion Analysis and Manganese-Iron Oxide Mineralogy of Quartz-Chalcedony Geodes from the Parana Basalts, Rio Grande do Sul, Brazil

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Introduction

Geodes are hollow bodies within rocks that are characterized by open space precipitation of minerals from the walls of the cavity inward. Many geodes are found in carbonate rocks although agate geodes are frequently found in vesicular volcanic rocks. Samples examined in this study were collected approximately 150km northwest of Pôrto Alegre in the state of Rio Grande do Sul, Brazil. They form within the Parana basalts which constitute the largest continental tholeiitic province of the world, with an area extent of 1.2 million square kilometers (Petri and Mendes, 1983). Thirteen separate lava flows (approximately 120 Ma) have been recognized (Amaral, *et al.*, 1966) with common mafic feeder dikes. Some flows are quite vesicular and over broad areas the vesicles have been variously silicified.

The purpose of this study is to document homogenization temperatures and salinities of primary and secondary fluid inclusions observed in quartz geodes and determine the mineralogy of non-silica phases. This information is synthesized with a number of previously published papers on geode and agate formation to determine a plausible origin for these objects.

Fluid inclusions have not been previously studied from this particular locality although Flörke *et al.* (1982) mentioned looking for them unsuccessfully in similar material. Matsui *et al.* (1974) studied the oxygen and hydrogen stable isotope characteristics on water-bearing “enhydros” from the study area and concluded the waters contained were of meteoric origin. Graetsch *et al.* (1985) studied stable isotope characteristics of water in chalcedony in agate geodes from the same geographic region. The presence of manganese oxide mineralogies in geodes from this region has not been published to the knowledge of the authors. Finkelman *et al.* (1972; 1974) described manganese and iron minerals contained in silica geodes hosted in volcanic rocks from the state of Chihuahua, Mexico. Constraints on the origin of those oxide minerals were not discussed.

Description of the Geodes

The geodes are of various sizes (3 to 7 cm in long dimension) and shapes (spherical, ellipsoidal, and “pinched” ellipsoids). A particular paragenesis of mineralization resulting in a specific geode stratigraphy, based on silica types, is identified. A nomenclature similar to Graetsch *et al.* (1985) was adopted for this study based on the similarity of sample types and geographic origin. Figure 1 presents two photographs of the different geode types, dark and light. All samples analyzed display mineralization only as wall lining.

The samples usually consist of a rim of opal-C that gives way to one or two of the three main types of chalcedony; milky white (Ch-m), translucent white (Ch-w), or translucent gray (Ch-g). Translucent gray chalcedony is characteristically on the outside portions of the dark geodes with the milky white variety in contact with microcrystalline quartz (MQ) toward the

interior. Light-colored geodes display a similar stratigraphy with the Ch-w present rather than the Ch-g. Interior to the translucent layers in both types, a thin layer of Ch-m is present immediately adjacent to MQ that is the next layer toward the interior. Flame-like structures of Ch-m flare out from the interior layers of Ch-m at the chalcedony-microquartz transition and approach the outer portions of the geode tangentially through the Ch-g and Ch-w in both light and dark varieties. The chalcedony is then replaced in the interior by a layer of MQ which then gives way to drusy, clear quartz crystals. Light-colored geodes are characterized by a greater abundance of crystalline quartz compared to the dark varieties. Some of the light samples consist almost entirely of clear quartz.



Figure 1. Dark (left) and light (right) geodes from the state of Rio Grande do Sul, Brazil.

Accessory manganese oxide minerals are present in both types of geodes. In dark types, two distinct morphologies are present; 1) large, black, and bladed crystals and 2) blue-gray tufts of acicular habit. In light-colored geode types, only the bladed morphology is present and is partially to totally covered by quartz crystals. All manganese oxide crystals project from the chalcedony-microquartz transition zone in the geode paragenesis.

Observations of the agate geode material under the microscope revealed a number of similarities and differences between the two geode types. In both types, fluid inclusions are found along the growth planes of quartz, most frequently near the MQ-quartz transition zone. Manganese minerals are found as concentric inclusions along botryoidal surfaces of layered chalcedony in the dark geodes and only rarely in light geodes. The manganese inclusions are concentrated along each growth interval in chalcedony, at the top of the layer. The chalcedony is oriented such that the long axes are perpendicular to the geode walls. Iron oxide staining, observed as small blebs in chalcedony, imparts the orange-yellow color to the light geodes. Oxide minerals were also observed between quartz grains in both types, although more commonly in the dark geodes.

Mineralogy of the Accessory Minerals

The most common crystal habit is large, 2-5 mm long, dark gray blades with a metallic luster. X-ray diffraction and energy dispersive spectroscopy on a scanning electron microscope (SEM-EDS) indicates the mineral to be pyrolusite. Pyrolusite crystals were largest, though fewer in number, in most of the light-colored specimens. Pyrolusite was also most common as inclusions in chalcedony in the dark samples. A second gray-blue mineral, with a more fibrous to acicular habit, was identified only in the dark geodes. X-ray diffraction coupled with compositional data from SEM-EDS identified this mineral as hollandite. Goethite was identified in the light colored geodes as inclusions in quartz and chalcedony.

Fluid Inclusion Analysis

All thermometric determinations were accomplished on a gas flow-type apparatus on doubly

polished fluid inclusion plates. Homogenization temperatures and salinities were determined by standard techniques. Fluid inclusions were only observed in quartz, most commonly at the quartz-chalcedony or quartz-microquartz boundary zone near the interior of the geodes.

Two types of fluid inclusions were observed at room temperature conditions; a one phase, liquid type (Type I) and a two phase gas and liquid type (Type II). Both types of inclusions were found isolated, along growth planes, or along healed fracture planes in quartz. The inclusions were restricted to quartz and most often found devoid of inclusions.

Type I inclusions were the most commonly observed type, occurring in both fractures and growth planes in quartz. Type I inclusions were most abundant in the dark geodes. Supercooling of the inclusion during salinity determinations occasionally resulted in the formation of a vapor bubble that would disappear upon subsequent heating to or above room temperature. Not all type I inclusions exhibited this behavior, however. A comparison of homogenization temperatures and salinities for type I inclusions in dark geodes are presented in Fig. 2.

Type II fluid inclusions were much less common and restricted to only the light-colored geodes. Type II inclusions were usually isolated or confined to growth planes and were occasionally found along fractures in the quartz. Results of homogenization temperature and salinity determinations for type II inclusions in light-colored samples are presented in Fig. 2. Individual fluid inclusion determinations are provided in Table 1.

One sample, with characteristics similar to both dark and light geodes, was noted with fluid inclusion homogenization temperatures intermediate between light and dark types. This “hybrid geode” also contained the lowest salinities documented.

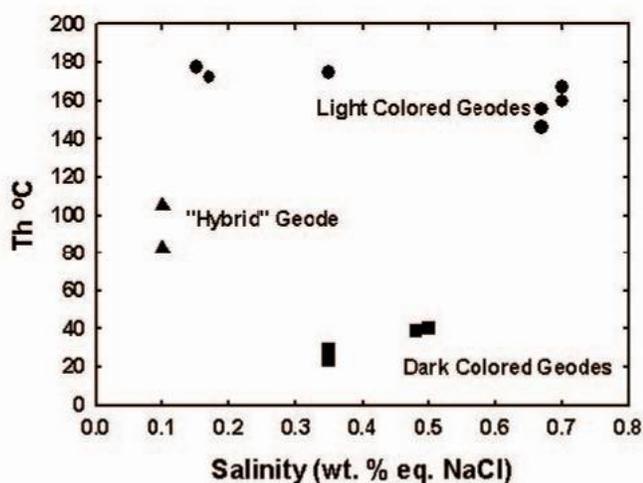


Figure 2. Plot of homogenization temperature (T_h) and salinity for different types of Rio Grande do Sul Geodes.

Origin of the Geodes

A number of papers have proposed mechanisms for the formation of agate and agate geodes. Mechanisms range from high temperature deposition of agate from supercritical fluids greater than 374°C (Flörke *et al.*, 1982) down to low temperature deposition of quartz from aqueous solutions at temperatures below 50°C (Fallick *et al.*, 1985). Graetch *et al.* (1985) inferred a formation temperature for chalcedony in geodes (similar to those of this study) at temperatures less than 250°C based on hydrothermal alteration experiments that resulted in modification of the mineralogy of the samples. Fallick *et al.* (1985) and Harris (1989) utilized hydrogen and oxygen isotope compositions to determine agate formation temperatures of 50°C and 120°C respectively. Flörke *et al.* (1982) and Graetch *et al.* (1985) also used infrared spectroscopy to determine the chemical nature of water in geodes and agate.

Results from the fluid inclusion analysis of the geodes in this study support the conclusions of a number of the studies mentioned above, despite the wide range of physiochemical variations inherent in each. The two fluid inclusion types observed in this study consist of a low temperature group (dark geodes) and a higher temperature group (light geodes). The color, accessory mineralogy, and structure of the geodes indicate two possible modes of formation or potentially a later alteration effect superimposed on the geodes of the Rio Grande do Sul region.

Table 1. Fluid inclusion determinations of quartz from agate geodes.

Sample Number	Inclusion Type	Homogenization Temperature (°C)	Salinity (eq. wt. %NaCl)	Geode Type
H-8	II i	172.3	0.17	light
	II i	174.6	0.35	
	II g*	167.1	0.70	
	II g*	146.2	0.67	
	II g*	155.6	0.67	
J-4	II g*	159.8	0.70	dark
	I g	23.8	0.35	
K-9	I g	29.5	0.35	light
	II i	82.5	0.10	
I-5	II i	105.0	@	dark
	I g	40.3	0.50	
B-4	I g	39.4	@	light
	II i	177.5		

i = isolated inclusion

g = growth plane inclusion

* = same growth plane

@ = freezing determination could not be accomplished

Low Temperature Origin:

The majority of fluid inclusions in the geodes studied were single phase, type I inclusions found most abundantly in dark geodes (samples J-4 and I-5). When homogenization temperatures could be measured, they were characteristically low ($< 50^{\circ}$ C) and of low salinity (Fig. 3). These values correspond well to the results of Flörke *et al.* (1982) calling for a final deposition of quartz from low temperature, low salinity solutions probably of low silica supersaturation. Such fluids were derived from meteoric or diagenetic processes and precipitated chalcedony and quartz as geodes in the vesicles. In addition to dissolved silica, the fluids also dissolved manganese and precipitated Mn oxides in the geodes. These fluid characteristics also correspond well to fluids analyzed from “enhydo” geodes by Matsui *et al.* (1972). In addition, the homogenization and salinity data of geodes analyzed in this study are similar to those reported by Roedder (1979) for geodes from sedimentary rocks. The lack of an iron phase in these dark geodes suggests iron removal from the system and may indicate geode formation as part of a pedogenic process.

Isotopic work by Fallick *et al.* (1985) and Harris (1989) suggests a low temperature origin for the formation of chalcedony as well. Fluid inclusion evidence does not support a boiling fluid as a silica precipitation mechanism as proposed by Harris (1989). No vapor-rich inclusions were observed in any portion of the quartz. Such inclusions would suggest boiling. However, the precipitation of chalcedony from boiling solutions cannot be discredited on the basis of fluid

inclusions observed only in late quartz.

High Temperature Origin:

Although a low temperature origin for agate geodes is supported by fluid inclusion data in dark geodes, higher temperature fluid inclusions were observed in the light colored varieties. In addition to differing color and fluid inclusion homogenization temperatures, the accessory Mn-oxide crystal morphology is characterized by larger, yet fewer crystals in the light-colored geodes. The general paragenesis of the silica types is similar except for the lighter color and presence of orange staining in the samples with high fluid inclusion homogenization temperatures. Quartz also tends to be more abundant in the light-colored samples. Higher fluid inclusion homogenization temperatures, dissolution of Mn oxide from chalcedony, and light color may indicate alteration of geodes by a higher temperature event. Hydrothermal alteration experiments on Brazilian geodes by Graetch *et al.* (1982) produced a whitening of chalcedony and the conversion of OH structural elements to water. The abundance of Ch-w and lack of Ch-g in light colored geodes may be a manifestation of a hydrothermal event sometime during and after formation of the geodes. Graetch *et al.* (1985) reported temperatures as low as 150° C was sufficient for this to occur. This recrystallization and dehydration of chalcedony probably produced the higher temperature fluid inclusion homogenization temperatures in a process similar to that described by Sander and Black (1988) for growth-zoned vein quartz in epithermal systems.

Primary precipitated chalcedony (formed at low temperatures) recrystallizes to quartz that will then contain pseudoprimarily fluid inclusions of anomalously higher temperatures. This process of solution and reprecipitation of silica mineralogies was described by Williams *et al.* (1985) and could result independently of increased temperature (which would only speed the transformation reactions) under conditions of burial and diagenesis. Essentially, this higher temperature geode group is the result of a closed-system reequilibration event either by hydrothermal alteration or by deep burial and silica reequilibration. The variable manganese oxide mineralogies also support differing histories of mineralization. Dark geodes represent “primary” formation and light-colored geodes represent “altered” types with recrystallized quartz and pyrolusite.

In order to discriminate between a hydrothermal event or burial, the geologic relationships of the geodes must be better known. This area from which the geodes came should be studied to determine if the light colored varieties are centered about a hydrothermal source or if the two types represent differing amounts of burial. The paragenesis of the geodes suggests formation during progressive burial in a sequence: opal → chalcedony → quartz, as described by Williams *et al.* (1985). However, the presence of Ch-w at the expense of Ch-g suggests hydrothermal alteration and would also correlate to the consistent high temperature homogenization temperatures observed in the light-colored geodes.

Conclusions

Two distinct types of agate geodes were identified from the Rio Grande do Sul region of Brazil. The different geode types could be distinguished on the basis of color, accessory manganese oxide mineralogy, silica mineralogy, and fluid inclusion homogenization temperatures. The differences between the two types of geodes are of secondary origin. The

geodes formed initially at low temperatures and the light-colored group underwent either a hydrothermal alteration event or greater burial with subsequent transformation of silica mineralogies through diagenesis. These secondary processes resulted in the bleaching of the chalcedony, manganese dissolution and recrystallization, and the recrystallization of quartz from chalcedony that resulted in the formation of higher temperature fluid inclusions.

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Seven Causes of Color in Banded Agates

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Banded agates occur at hundreds of localities around the world. Although the size and shape of agates from several different localities can be very similar, the color of agates from a particular locality is often distinctive. The color (or more importantly the combination of colors) agates exhibit often allows an experienced observer to correctly attribute an agate to a specific locality. Color is, therefore, an inherent property of all banded agates and is one of the primary characteristics affecting their aesthetic appeal and monetary value. Examples of the wide variety of colors exhibited by agates can be found in Carlson's (2002) book on banded agates.

Color in Agates

The color (or combination of colors) a particular banded agate will exhibit is dependant on seven basic factors:

- 1.) The inherent color, clarity, and porosity of the chalcedony layers that make up most bands.
- 2.) The color, chemical composition, and size of iron, manganese, and iron-bearing manganese mineral inclusions within the chalcedony bands.
- 3.) The degree to which these mineral inclusions, within chalcedony bands, have been altered by invading water.
- 4.) The iron content of invading water.
- 5.) The color of quartz crystal layers between or adjacent to chalcedony layers.
- 6.) Special optical effects caused by diffraction, and fluorescence under ultraviolet light.
- 7.) Late-stage weathering products and/or surface coatings incorporated into chalcedony layers.

Each of these factors can, and often does, affect the other factors, and in turn the colors a given agate will exhibit. Our research has shown that the colors that a particular agate now exhibits, is not necessarily the same colors that were present when the agate first formed.

Color of Chalcedony

Chalcedony (fibrous micro-crystalline quartz) occurs in a variety of shapes, sizes, and colors within banded agates. In the context of the coloration of banded agates, we have simply divided chalcedony into three basic types, based mainly on observation of hand specimens under low power magnification (10-40x).

White Bands

Opaque, relatively wide, concentric white bands are a common feature in hand specimens of agate. The bands can be as much as .20 inches wide and consist of very straight and tightly packed chalcedony fibers. The fibers appear to have few structural defects and there are few water-filled cavities within the white chalcedony layers. The layers have very low porosity and

permeability and are not susceptible to the infiltration of late-stage fluids (water) or artificial dyes. Although opaque in hand specimens, these layers are transparent in thin section.

Colorless Bands

Transparent, colorless, chalcedony bands are also a common feature of banded agates. On a hand specimen scale the layers can be fairly narrow or quite wide. On a microscopic scale the fibers appear to be relatively short, twisted, and contain small fluid (water) filled cavities. These bands often host large numbers of manganese and iron-bearing mineral inclusions. The transparent bands are also moderately porous and permeable, and are susceptible to the infiltration of ground water (iron and non iron-bearing) as well as artificial dyes. When narrow bands of colorless chalcedony are sandwiched between bands of opaque white chalcedony, the colorless bands can appear black or dark grey.

Milky-White / Blue-Grey Bands

Translucent, light blue-grey to milky-white bands are, in most respects, very similar to the colorless bands, except that they are more translucent. The reduced clarity is apparently due to the large numbers of small, pervasive (water-filled) cavities scattered throughout the chalcedony. The blue color, sometimes exhibited by these translucent layers, has been attributed by Pelto (1956) and others to the scattering of light by these small cavities. This phenomenon has been referred to as Rayleigh scattering, and occurs when the particle size of a cavity or mineral inclusion is smaller than the wavelength of visible light.

When the cavities become larger than the wavelength of light, the chalcedony loses its blue color and appears a translucent milky white. This is similar to what causes the white color in milky quartz crystals. A good discussion of this and related topics can be found in Fritsch and Rossman (1988). The blue-grey to milky-white bands often contain many manganese and iron-bearing mineral inclusions, have a relatively high porosity and permeability, and are susceptible to the infiltration of late-stage water and/or artificial dyes.

Mineral Inclusions

Iron- and manganese-bearing mineral inclusions (both unaltered and altered) are responsible for most of the color observed in banded agates. Although trace element studies by Harder (1993), Götze et al. (2001), and Flörke et al. (1982) indicate the presence of cobalt, lithium, sodium, potassium, chromium, arsenic, titanium, etc., these elements appear to have little or no effect on the color of banded agates. Our research has shown that the only significant coloring agents in banded agates are iron and manganese. We will first discuss unaltered, then altered, iron, manganese, and iron-bearing manganese mineral inclusions.

Iron Minerals

Unaltered iron oxide/hydroxide mineral inclusions are very common in banded agate. In fact, they are so common that early researchers believed that iron “triggered” the rhythmic precipitation of chalcedony found in banded agates. Work by Moxon (1996a,b) and others showed this to be untrue. The oxidation state of iron in most natural environments is either +2 (ferrous) or +3 (ferric) and results in a variety of iron oxide and hydroxide minerals, most of which could potentially occur in banded agates. The most common iron-bearing minerals in banded agates appear to be hematite and goethite.

Small red mineral inclusions in banded agate are common and are presumed by most casual observers to be hematite. While this is most often true, we feel that red goethite, lepidocrocite, and ferrihydrite are also possibilities, and care should be taken in applying mineral names to inclusions based on color alone.

In his well-written articles, Finkleman et al. (1972, 1974a, b) listed a wide variety of iron and manganese minerals that he found in the central cavity in Mexican geodes (the outer shell of which is often banded agate). He reported that hematite in the central cavity occurred as rounded platy crystals and rosettes of black, red, orange, brown, and green color, whereas goethite occurred as blades, rods, and plates of black, red, orange, and brown color. He also reported that the small hematite and goethite crystals were often intergrown and/or perched on each other. The variety of possible crystal shapes and colors exhibited by hematite and goethite, their small size, and the variable transparency of the chalcedony layers, makes the accurate visual identification of individual iron-bearing mineral inclusions very difficult, without the use of a scanning electron microscope and other sophisticated instruments and techniques.

Lavender Color

Although originally attributed to manganese, researchers now believe that most (if not all) lavender color in chalcedony is due to iron. Several different mechanisms are capable of producing the purple color. The first mechanism involves small dark-orange to red, iron-bearing inclusions hosted in blue chalcedony (caused by Rayleigh scattering). The eye (by optical mixing) perceives the combination of colors as various shades of lavender. This effect has been described by Lentz (1999) in agate-filled thunder eggs from St. Egidien, Germany. We have also observed this phenomenon in agates from St. Egidien, as well as in a few agates from northern Mexico. A similar effect occurs when small inclusions of light-reddish, iron-bearing minerals are hosted in layers of light grey (fairly transparent) chalcedony. The color produced by this mechanism can be a medium to dark purple. The cause of the grey color in the chalcedony layers is undetermined, but could be due to finely disseminated iron or manganese. Agates from certain localities in northern Mexico, as described by Cross (1996), exhibit this type of lavender coloration.

Another coloring mechanism involves an “amethyst-like” effect caused by iron, as described by Shigley and Koivula (1985) in purple chalcedony from Arizona. We believe the pinkish-purple chalcedony from Creede, Colorado is due to a similar cause. The exact mechanism of this amethyst-like effect in chalcedony, however, is not fully understood.

Altered iron oxide/hydroxide minerals (hematite/goethite) are responsible for much of the bright red, orange, and yellow coloration exhibited in highly colored banded agates. Although primary (unaltered) red hematite inclusions are common in agate, much of the hematite (and goethite) is deposited as black-colored, crystal inclusions in agate. Since most of the colorless, translucent white, and blue-grey chalcedony is porous and permeable, shallow ground water can easily enter and travel through these porous agate layers. When the oxygenated ground water encounters black iron-bearing minerals, they are often altered to a more oxidized and hydrous (colorful) form.

Many agates show zones of unaltered (black) mineral inclusions on one side of the agate, and highly altered (colorful) inclusion-filled zones on the opposite side. The line of demarcation, where the colorful and the black zones meet is often quite sharp. The size of the inclusions is the same on either side of the line of contact of the black and colorful inclusions. We interpret this to show how near-surface waters can sometimes invade an agate from one side and travel only part-way through it, altering iron-bearing minerals in the part invaded by the ground water to a bright color. Parts of the agate not invaded by the ground water retain their original, unaltered (black) color. We believe this phenomenon has been incorrectly attributed to chromatography by many authors.

The color exhibited by altered iron oxide/hydroxide inclusions is dependant on (1) how oxygenated the invading waters are, (2) how thoroughly the agate is flushed, and (3) the crystal size of the unaltered inclusions. Although it is hard to quantify the first two factors, the last factor (crystal size of inclusions) is easily observable. With all other factors being equal, small mineral inclusions become more completely altered than large inclusions. Generally, the smallest, most altered inclusions will appear yellow, the next larger size will appear light orange, and the largest size will appear various shades of dark orange or red and will often have a core of unaltered (black) iron oxide/hydroxide. Although the full range of colors is seldom exhibited in a single agate, notable examples from northern Mexico can be spectacular.

Iron-bearing Water

Dissolved iron in the water that invades a particular agate can also “stain” porous agate layers various colors. Generally, the higher the iron content and less oxygenated the water the darker the color. Many of the natural, light-orange to dark-brown agates from Brazil show this phenomenon well. Most of the coloration in the agate-filled thunder eggs from the Baker Ranch locality, in southern New Mexico, is also due to the invasion of iron-bearing waters (of various concentrations) into colorless chalcedony layers.

Manganese Minerals

Unaltered manganese oxides and hydroxides commonly occur in banded agates to varying degrees. Agates hosted by acidic to intermediate volcanic rock (rhyolite and andesite) often have relatively large amounts of manganese oxide/hydroxide inclusions, while those hosted by basalt and sediments appear to have fewer manganese-bearing inclusions.

Nearly all manganese oxides and hydroxides are black or dark brown, and are often difficult to visually distinguish from unaltered iron oxide/hydroxide inclusions. The articles by Finkleman et al. (1972, 1974a,b) list and show good photos of seven manganese oxides/hydroxides, and we feel these are good candidates for inclusion in banded agate layers. Our research has shown that romanèchite should be added to the list. We feel that the most likely candidates for inclusion in banded agates are: romanèchite, todorokite, birnessite, cryptomelane, and hollandite.

Altered “pure” manganese oxide/hydroxide inclusions are conspicuous because of their apparent absence in banded agates. Under nearly all natural earth-surface conditions, manganese oxide and hydroxide minerals are very soluble in surface and ground waters, and can be easily flushed out of porous chalcedony layers in banded agates. The manganese bearing inclusions are so soluble that when water flushes through a black, inclusion-rich zone, all that is left of the original

black inclusions is a series of hollow cavities that appear as white specks to the unaided eye. The white color is due to the “frosted” nature of the chalcedony walls surrounding the small hollow cavity, and also to an unidentified powdery white substance that partially fills many of the small cavities. Many fine examples of this phenomenon are provided by the dissolution of romanèchite in the agate-filled thunder eggs at the Baker Ranch locality in southern New Mexico. We have also observed this phenomenon in several banded agates from Brazil.

Iron-bearing Manganese Minerals

Unaltered iron-bearing manganese minerals, to the best of our knowledge, have not been previously reported within banded agate layers. Our research has shown that, iron-bearing manganese minerals do exist in banded agates and may be (in their altered form) a strong coloring agent in banded agates. To date, we have only found one species of iron-bearing manganese oxide (*i.e.*, romanèchite) in banded agate, but we feel that iron-bearing todorokite and hollandite are also good possibilities. We have recognized unaltered iron-bearing romanèchite in the so called “Condor” agates from Patagonia (Argentina), and we believe that it and/or iron-bearing todorokite may also occur in Brazilian agates.

Altered iron-bearing romanèchite can act as a very strong coloring agent in banded agates. Our examination of strongly colored “Condor” agates from Patagonia indicates that most coloration is due to the dissolution of iron-bearing romanèchite and the transfer of colorful “amorphous” iron oxides to the surrounding chalcedony layers. The type and strength of coloration of the chalcedony layers is believed to be directly related to the iron content of the original iron-bearing romanèchite inclusions. The brightly colored yellow, orange, and (some) red coloration in chalcedony layers in “Condor” agates is directly attributable to the dissolution of iron-bearing romanèchite and the redeposition of “amorphous” iron oxides in the enclosing chalcedony layers. We have observed a similar phenomenon in some agates from Brazil.

Quartz Crystal Layers

Bands of anhedral crystalline quartz, sandwiched between layers of white chalcedony, are a common feature in banded agates. Taijing and Sunagawa (1994) have investigated these quartz crystal layers in detail and have shown that these layers are the final stage of “normal” growth of the chalcedony fibers. The quartz crystals in these layers are almost always colorless. The only exception we have observed is the light-colored amethyst crystal layers in “sowbelly” agate from Creede, Colorado. The interior of many banded agates contains a central core of late-formed crystalline quartz and often have euhedral quartz crystals projecting into an open cavity. These crystals are most often colorless or purple (amethyst). Brown (smoky) quartz is much less common, and yellow (citrine) crystals are rare. Black quartz crystals, due to the inclusion of the manganese mineral, todorokite, have been reported by Finkleman (1974) in crystal-lined cavities in geodes from northern Mexico. We have also observed these in small agate geodes from Brazil.

Special Optical Effects

Iris agate results from a rainbow-like effect that occurs when sunlight or incandescent light is viewed through a thin slice of transparent, finely banded agate. The rainbow effect is caused by narrowly spaced chalcedony layers, each with a slightly different index of refraction, acting as a diffraction grating and breaking the light up into its spectral colors. This phenomenon is well described by Jones (1952), and by Heaney and Davis (1995).

Transparent and translucent layers of chalcedony in many agates fluoresce a bright, chalky-green color under short wave UV (ultraviolet) light due to the presence of uranyl ions in small fluid-filled cavities. Some chalcedony layers also fluoresce a bright white color under long wave UV light, due to an undetermined cause. These bright white fluorescent layers appear to occur most commonly in chalcedony that contains white specks (cavities) that were previously occupied by non iron-bearing romanèchite.

Late Stage Weathering / Surface Coatings

All banded agates, when exposed to earth-surface conditions, will exhibit the effects of weathering to a greater or lesser degree. Highly weathered agates (and petrified wood) often exhibit a chalky white outer layer composed of opal and a small amount of clay. In extreme cases, all banded zones can be completely altered to a chalky white color.

Iron-bearing agates, when exposed to sunlight (heat) at the earth's surface, will often turn from a dull yellow-orange color to a bright red. This is due to the dehydration of hydrous iron-bearing mineral inclusions. Surface coatings of manganese and iron oxides, analogous to "desert varnish", are occasionally seen on the surface of some agates partially exposed to the atmosphere in arid regions. Agates collected from iron-rich till or soil can have a thin coating of red iron oxide on their surface. In extreme cases, the iron can penetrate deeply into porous chalcedony layers.

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**Very-High-Temperature, Closed-System Origin of Agates in Basalts:
A New Model, New and Old Evidence**

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Crystallization of the self-organizational, *repetitive* chalcedony textures (Fig. 1) and trace-element compositions typical of many agates theoretically requires that the growth be from a phase with huge silica concentration and very low silica self-diffusivity. Both requirements point toward agate crystallization from a blob of silica gel (Wang & Merino, GCA 1990, AJS 1995), and precludes crystallization of agate (with repetitive textures) from aqueous silica solutions at any temperature and pressure.

We have come up with the following picture to form blobs of hydrous silica gel within a basalt. All the predictions following from this picture are confirmed by observations of many kinds – isotopic, mineralogical, textural, microstructural, trace-element, dynamic, etc. – collected by others and by us.

Blobs of silica gel must form instantaneously if a hot basalt (1200 °C) flowing on the ground happens to trap water puddles: the water goes instantly supercritical, enters the flow from below, reacts with silica polymers in the melt, and forms silanol-ended silica polymer chains that via hydrogen bonds should attach to each other at T junctions – this *is* a hydrous silica-rich gel. There is independent experimental evidence (Doremus, 2002) that above 450 °C that reaction does take place. (First prediction: If gel blobs form by puddle trapping, agates should occur near the bottom of the basalt flow. Agates do occur only in the bottom 3 meters of a 14-meter-thick basalt flow/agate quarry that I visited in 1991 in the Parana Basalt at Rio Jacui, NW of Porto Alegre, Brazil, whereas the basalt vesicles, which occur only in the top meter, are still today all empty.)

The basalt flow stops moving and starts cooling down. As the 1000-degree isotherm sweeps inward through the flow, the basalt crystallizes fast. Each glob of silica gel, as a closed system, quickly crystallizes into an agate too, just as fast as the surrounding basalt, and at a similar, very high temperature. (The high growth rate predicted independently from the self-organizational crystallization model of Wang & Merino, 1990, coincides with the high rate predicted now similar to that of the surrounding basalt.)

Because this is a silica gel, the basic condition for it to develop repetitive textures is satisfied. Trace elements and silanols in the gel get mostly (not completely) segregated into the residual gel as the repetitive layers of chalcedony grow. Repetitive layering, fibrosity, alternate trace-element content, alternate $\delta^{18}\text{O}$, and alternate-band fiber twisting all are predicted to follow, as often observed, and must eventually give way inward to non-banded quartz, also as observed. (It's because the silanol and the trace elements do not get completely segregated to the residual gel that a) agates show an unusually high silanol content, as analyzed by Flörke et al. in 1971; and that b) agate chalcedony contains a little nickel in solid solution.) Predicted see-saw $\delta^{18}\text{O}$ values were indeed detected by Savin, Case Western Reserve University.

The last quartz (often coarse amethyst) grows when trace iron has been forced to become both concentrated and oxidized (through the awesome reaction $\text{Fe}^{++} + \text{H}_2\text{O} = \text{Fe}^{3+} + \text{OH}^- + 0.5\text{H}_2\text{O}$). This explains both why the last quartz is darker and darker amethyst (Fig. 2) and why it may contain coprecipitated fibrous goethite (Fig 3). All this should happen at very high temp. Indeed, we have measured the $\delta^{18}\text{O}$ fractionation between the amethyst and the goethite; the two minerals differ by only about 1.5 ‰, confirming that the crystallization of both was at several hundred degrees C, say, 800 °C plus/minus 100 °C. The silanol water of the initial gel blob collects as H₂O water in the agate's central void, itself resulting from the density difference between gel and quartz.

The chalcedony layers *should* be high in $\delta^{18}\text{O}$ – as they indeed are – but it isn't because they have crystallized from low-temperature water as Fallick (1985) assumed and (circularly) “proved.”

Eventually, when the cooling of the agate (and the basalt it is in) proceeds down to 350-400 °C and crosses the boiling curve of water, the Fe- and Ni-bearing, fairly heavy ¹⁸O water accumulated in the center of the agate leaks or flashes out, and should isotopically alter a shell of basalt around the agate in a declining gradient. Indeed, in a sample of fresh Deccan basalt + agate we have measured $\delta^{18}\text{O}$ values of: 16.6 ‰ at the edge of the agate, 9.5 ‰ in basalt at 2 mm from the agate, 9.2 ‰ at 1 cm, and 6.7 ‰ at 1.9 cm from the agate - that is, down to fresh basalt. Each agate produces its own small “centrifugal” aureole of isotopic alteration, even in a fresh basalt.

That same flashing water may – thanks to its high pH – alter a film of surrounding basalt to zeolite, as often observed. (Zeolites stuck to agates were the only zeolites known prior to 1955, when sedimentary zeolites and zeolitites were discovered.)

Back to the fibrous and twisted chalcedony layers: soon after growing, twisted quartz fibers start to anneal – that is, they start to resolve their strain into twins and dislocations. This is when the huge submicroscopic dislocation density characteristic of agates (including the highly Brazil-twinned moganite) is generated, with the fibers and the twisting remaining observable on an optical scale.

When the puddle of water that gets initially trapped by the basalt flow is large then a huge lump of low-silica-concentration gel forms. Because this gel is low-density, both the lump will stretch itself vertically and it will generate only very few repetitive bands before passing to nonbanded, non-fibrous coarse amethyst, and the agate's central hollow will be large relative to the whole agate. This is exactly what the large “geodes” that one can walk into look like: bottle-shaped, having very few chalcedony bands, and lined with big amethyst crystals.

The same 1995 theoretical quantitative model that accounts for the self-organizational textures and compositions of agates and for their fibrous, length-fast quartz also accounts for a score of geochemical, mineralogical, microstructural, isotopic, and chromatic features of agates.

Summary. Agates probably crystallize from lumps of gel formed at very high temperature within a basalt flow, as the flow traps a puddle, or water soaking the ground. The crystallization of the gel lump to form an agate takes place at roughly the same high temperature, fast rate, and time as those for the surrounding basalt. As each agate crystallizes one predicts that it will form a directional sequence of textures (alternate chalcedony bands, non-banded non-fibrous quartz with increasingly darker amethyst, and a center void); all this is exactly as seen. Coprecipitated

amethyst and goethite show little fractionation, confirming the very-high-temp of crystallization predicted by the geological model. Predicted flashing of water accumulated at an agate's center should isotopically alter surrounding basalt in a declining pattern of delta 18-O values; this is nicely confirmed by measured values.

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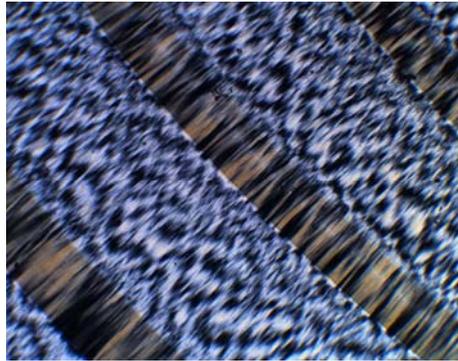


Fig 1: Repetitive alternating chalcedony bands, with fibers twisted and non-twisted: a tremendous case of self-organization



Fig 2: Increasingly darker purple of amethyst: best single evidence of closed-system growth



Fig 3: Ferric iron segregated to the residual gel/aq soln during xln of an agate makes the coarse quartz (increasingly darker) purple *and* also precipitates out as goethite bundles. 18-O fractionation between goethite and amethyst is only 1.5‰, evidence that both crystallized at many hundreds of degrees.

Stratigraphic Distribution, Environments of Deposition, and Formation of Agate in the Buck Hill Volcanic Series, Brewster County, Texas

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Examination of numerous agate nodules and their stratigraphic settings show that they are usually confined to five lithologies ranging from volcanic rhyolitic ash flow tuffs, tholeiitic basalts and andesites to marine carbonates and siltstones. A model for the origin of the plume agates found in the Eocene-Miocene basalts and andesites of the Buck Hill alkaline Volcanic Series of West Texas have been developed. Agatization is a secondary process that shows the history of erosion. No silica from hydrothermal processes was found in the area to account for the volume of agates. There was no evidence of hydrothermal alteration or propylitization of rock.

Agates are diagenetic products that come from the dissolution of volcanic ash into silica gels. Acidic rocks (tuffs and volcanic ash of the Duff Tuff, Tascotal Tuff and Mitchell Mesa Rhyolite) that overlie basalts and andesites (Sheep Canyon Basalt, Cottonwood Springs Basalt, and Potato Hill Andesite) are altered to clays, zeolites, and silica gels. The basic formula for secondary agatization is: ash flow tuffs/ volcanic ash + devitrification/weathering + water in a high (alkaline) pH environment yields siliceous gel (monomeric silicic acid $H_4SiO_4 + H_2O$) + clay (montmorillonite) + zeolites (clinoptilolite). Small remnants of the white montmorillonite/clinoptilolite deposits are found throughout the area stratigraphically overlying the basalts and andesites. Silica is highly soluble in water at near surface conditions (c. 25 degrees Centigrade at 1 atm) at a high pH (near the highly alkaline pH of 8). Evidence of the highly alkaline environment is the presence of fresh water limestone beds interbedded with the Sheep Canyon Basalt flows. With the dissolution and devitrification of the stratigraphically higher volcanic ash/tuffs/ash flow tuffs into silica gels, the gels enter the groundwater system by percolating and collecting in the vesicles of the underlying basalts/andesites. With exposure the agate nodules hydrate and harden. The water table movement and erosional history is depicted in the banding and plumes of the agates. The oldest agates of the Lower Sheep Canyon Basalt have distinct banding (depicting "chemical aging") and were exposed last. The agates of the Upper Sheep Canyon Basalt show vertical plumes, stalk aggregates, stalactites, and tubes showing the fluctuating movement of the water table. The horizontal plumes of the Cottonwood Springs Basalt show the water table horizon and were the first agates to be exposed.

The silica molecules dispersed within water form a sol (10^{-7} to 10^{-3} cm in size) and are negatively charged. As electrolytes are added, the sol or gel is neutralized and the gels begin to flocculate and harden (syneresis). The plume agates that are formed are a result of the reaction between the hematite or limonite formed from the weathering of the basalts and andesites. These metallic oxides form the plumes or banding within the silica gel and are the impurities found in the gel. The reaction also produces the spherulitic crystal growth indicative of chalcedony. Thus, banding is a precipitation of impurities within the siliceous gel and is not a rhythmic occurrence. Pseudomorphs/molds of aragonite, calcite, gypsum, anhydrite, barite, zeolite and calcite are precursor and contemporaneous minerals (indicative of saline/alkaline environmental conditions)

that were present before the gel arrived, are incompatible with the silica gels and do not react with the sol to produce plumes and banding. Thus, silica undergoes transformation from a highly saturated orthosilic acid gel to opal (no crystalline structure with much water) to chalcedony (spherulitic growth). Euhedral quartz growth, also commonly found in agates, forms when the agate nodule becomes under saturated with respect to orthosilicic acid.

The structure of the agates is also indicative of collomorphic or gel minerals. This usually takes the form of botryoidal shapes as defined by Lebedev. Other minerals that depict metacolloidal deposition are malachite, cassiterite, and hematite.

Idar-Oberstein and its Agate History

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Idar Oberstein is Germany's principal gem cutting and polishing center. For more than 500 years the history of the area was intimately interwoven with gemstones. The city is located along the Nahe river valley in the Hunsrueck Mountains in the German state of Rhineland-Palatinate.

The discovery of agate drew the developing gem industry to this region. The agates themselves formed in vesicular latitic-andesitic volcanic rocks emplaced during the Permian period "Rotliegend" about 270 million years ago. Smoky quartz, amethyst, jasper and calcite were also secondary products of this volcanism. The mines are now exhausted, but one mine at Galgenberg/Steinkaulenberg has been reopened for visitors.

The origins of gem industry were first documented in 1497, and the industry developed strongly in the 17th and 18th century. Grinding was carried out with water-powered, natural-sandstone wheels in stone-cutting mills, which were located along small rivers and streams. After some ups and downs, the gem industry peaked before the onset of World War I. At that time, several thousand agate cutters and grinders worked in the area. Cutting and polishing of agate was carried out in family businesses that were also actively engaged in farming.

When the deposits declined at the end of the 18th century many grinders and cutters emigrated. At the beginning of the 19th century large agate deposits were discovered in Brazil and in 1834 the first shipment was brought to Idar-Oberstein. In addition to cutting jewelry, stone articles for daily use like knives and forks, bowls, boxes, buttons, trading objects ("African money") and beads were carved. Today, cutting of imported gemstones, cameo master carving and production of modern lapidary art is the most important industry of the town (Figure 1).

The collection at the Mineral Museum of Bonn (Germany) contains some fine agates from the Idar-Oberstein region. These agates are dominated by soft pink, red and brownish colors (Figure 2).

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Fig. 1. Armin Franzmann, a modern-day cutter.



Fig. 2. Agate nodule from Idar-Oberstein with amethyst and pseudomorphs.

A History of Scottish Agates

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Over geologic time the landmass that was to become present day Scotland travelled from an initial position near the South Pole. During this complex geological past it underwent considerable changes and no other country for its size can boast rocks from all the geological periods. This created many different source rocks from which diverse minerals have been found. The Devonian, Carboniferous and Tertiary were periods of extensive volcanism. During these times there were huge outpourings of lavas and ash. It is these ancient lavas that are the host rocks for the vast majority of agates (figure 1).

Tectonic movements and erosion have shaped the present day landscape such that the remnant Devonian lavas are largely represented by low hills and the Carboniferous lavas by remnant volcanic plugs and occasional plateau lavas. The youngest lavas of the Tertiary period were extruded during the opening of the Atlantic Ocean. Despite massive erosion that has exposed the roots of the magma chambers of the enormous volcanoes there nevertheless still exist thick and extensive lava piles.

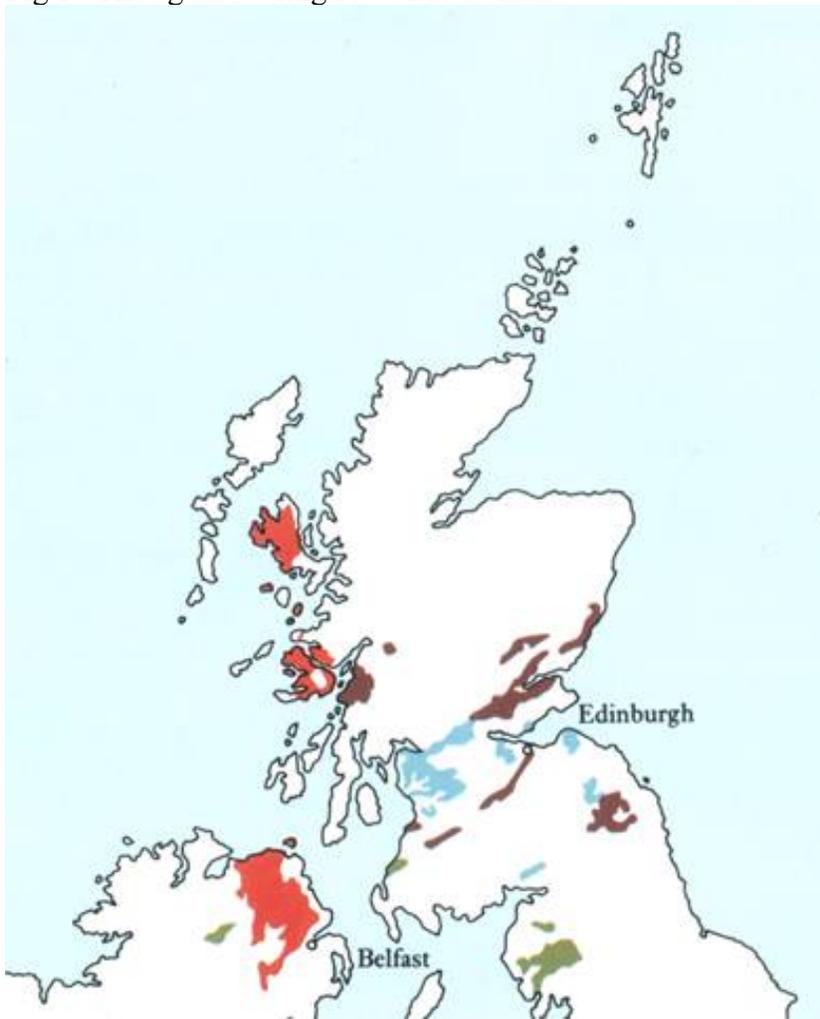
Each period has its own characteristic agates. The Devonian agates are the most prolific and show the greatest range of colours. Carboniferous agates are rare and more often the agate occurrence is as vein agate rather than vesicle-filling agate. The Tertiary agates are the least colourful, usually only found in pale shades of blue-grey with white bands. In Skye the Tertiary agate-bearing flows are often at the base of 300 m thick sequences of zeolite-rich lavas.

Within the Devonian lavas each locality gives rise to agates with distinctive features and colours such that the expert can often accurately establish the locality based solely on these attributes (figure 2). Many of the structural features are of significant interest in attempting to explain the origins of banding and agate formation (figure 3). Whilst the presence of silica rich zeolites such as mordenite is not uncommon in Devonian lavas, the Tertiary agates show a more intimate relationship with zeolites inasmuch as the zeolites often form a complete initial lining of the cavity. It is interesting to note that higher-temperature zeolites can occur in the lavas above the agate-bearing flows. These all impinge on issues such as the temperature of agate formation and the penecontemporaneous development of agates.

Because of the abundance of agates in Scotland, the problems central to agate formation have been considered by several notable Scots. Matthew Forster Heddle's (1828-1897) studies (figure 5) gave rise to his excellent publication on agate formation that was later included in his *Mineralogy of Scotland*. Heddle developed a sequence of vesicle-filling events and also proposals on structures such as stalactites, discoids, segregation features and the tube of escape which he believed was crucial in explaining agate formation. John Smith followed Heddle and in his publication, *The Semi Precious Stones of Carrick*, he presented his own theories based on

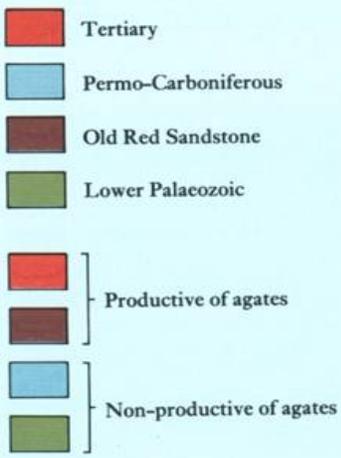
his observations on thousands of agates. These differed little from those of Heddle but he added unusual explanations for some structures, particularly twisted stalactites (figure 4) the forms of which he attributed to the effect of Galvanic forces. Harry Macpherson (1925 – 2001) is perhaps the last of the Scots to have published a theory on agate formation. He, like Smith before him, drew largely on Heddle's ideas and observations, refining them in the light of modern published papers on agates and their formation. He particularly favoured the dynamic effects of crystallisation in the production of chalcedonic banding and features such as the tube of escape.

Fig 1. The agate-bearing lavas in Scotland



Key to Fig. 1

Key:



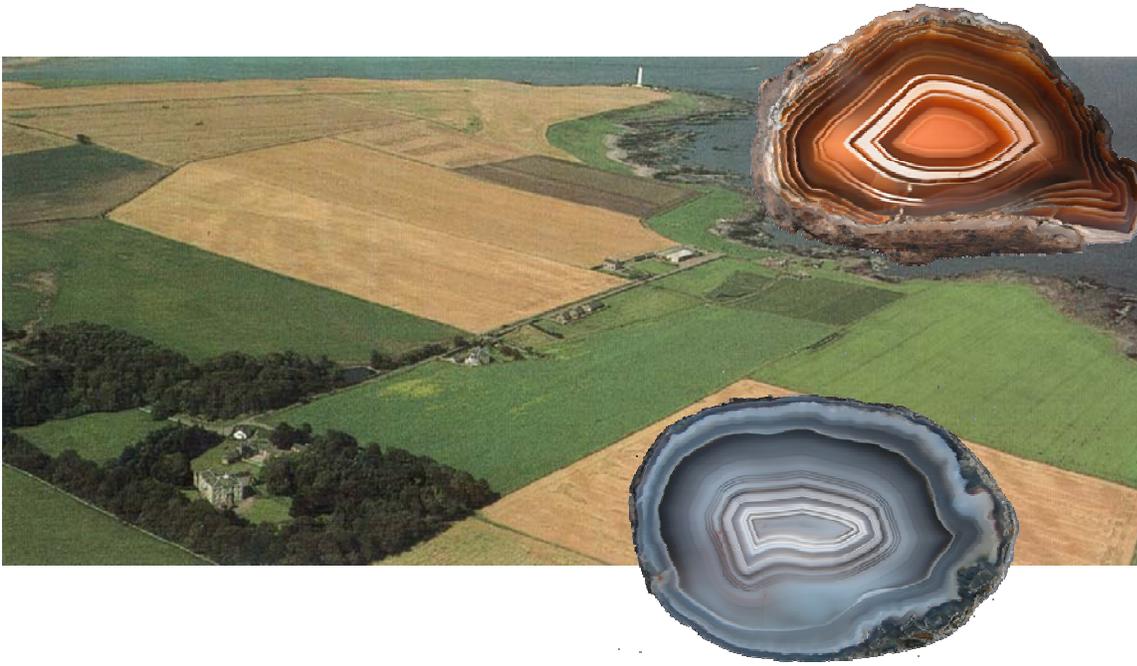


Fig. 2
The eroded Devonian lavas near Montrose, between Scurdie Ness lighthouse (top centre) and Usan (bottom left) and the agates characteristic of each locality.

Fig. 3

Agate showing many tubes of escape considered by Scottish writers on agates to be central to the explanation of agate formation.



Fig. 4
Twisted stalactites



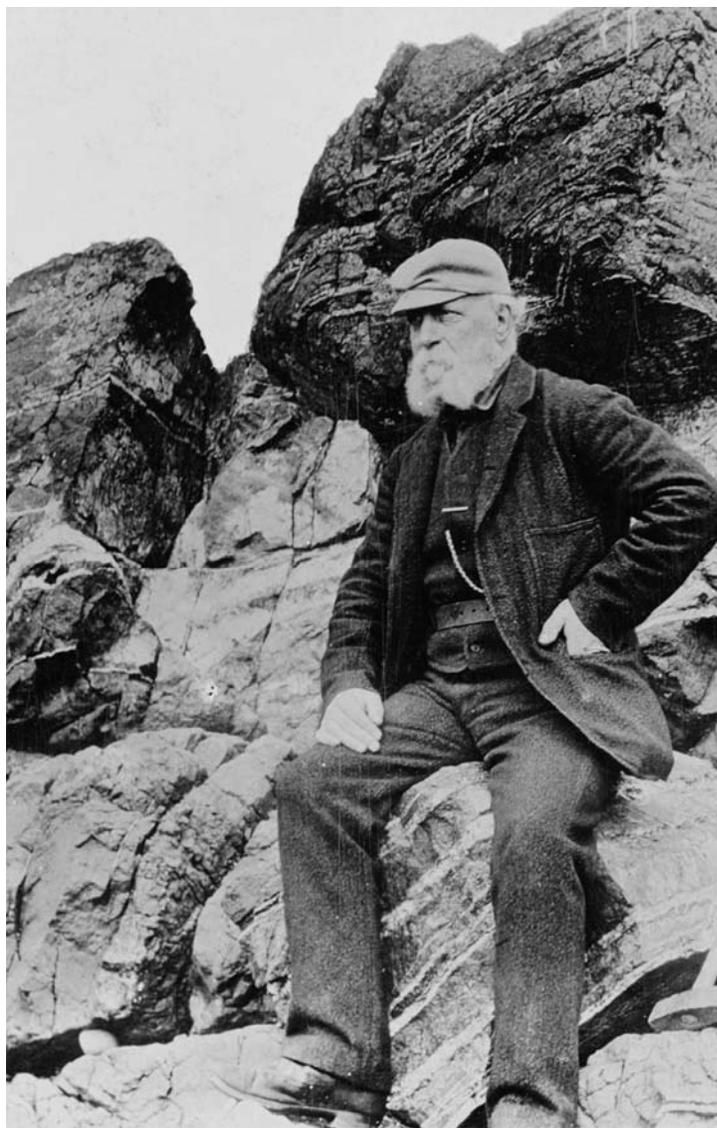


Fig. 5
Matthew Forster Heddle

Fairburn Agate: Occurrence in the Badlands, Grasslands and Black Hills of Southwestern South Dakota and Northwestern Nebraska

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Geologic history and determination of host formation

The Fairburn agate is a rare and exquisitely banded agate (a type of fortification agate) of sedimentary origin which was brought to the surface with its limestone host by the Black Hills uplift. Fairburn agates are distributed throughout the area to the south and east of the Black Hills, in alluvial deposits in the badlands and grasslands, and are also found in situ in the Black Hills, within outcrops of the Minnelusa limestone. Agates from these various locations have very different superficial appearances, which leads to much speculation about their origins. When they first came to the attention of collectors, the agates were being recovered from surface deposits of gravel near the small town of Fairburn, SD. The accompanying photo/slide exhibit is intended to demonstrate and document the geologic history of the Fairburn agate, the characteristics of the agate, the relationship to the host formation and its occurrence in that formation.

Prior to the uplift of the Black Hills, which began roughly 60 million years ago (mya), the Minnelusa limestone was at a depth of 5,000 feet below the surface. The Minnelusa had accumulated in shallow seas beginning during the Pennsylvanian Period and ended in the latter part of the Permian Period. The deposition took place over an approximate 50-60 million year time span beginning 310 mya and ending 250 mya. As the Black Hills uplift progressed, there was a disruption of the older stratigraphic units and the creation of new formations surrounding the Black Hills. Over 7,000 feet of rock were eroded and redeposited into the surrounding area. The geology was further complicated by ash fall from volcanic activity in the Rocky Mountains approximately 30 mya, which covered all but the top of the Black Hills.

The Fairburns in the badlands/grasslands area surrounding the Black Hills were found in association with the Chadron Formation. It had accumulated as alluvial deposits which had eroded from the Black Hills 34-44 million years earlier. This formation had, in turn, been buried under ash fall and more recent geological formations for a period of 30 million years, keeping the agates hidden from view. They were uncovered again in more recent geologic times when the erosion which created the South Dakota Badlands again brought them to the surface. As a result of a study of the Chadron Formation (LaGarry) in the late 1990's, the basal strata, consisting primarily of sand and gravel, has been renamed the Chamberlain Pass Formation.

The majority of Fairburn agates which are collected in the badlands/grasslands have evidence of host rock attached. However, the host consists of chert and gives no evidence of a limestone origin. This caused early collectors to conclude that Fairburns did not have a limestone origin. The action of being stream tumbled as they were eroded from the Black Hills had stripped the nodule of the limestone host and left only remnants of the chert and agate nodule. Completely

banded nodules are also found without either limestone or chert attached. The agate then is referred to as a solid agate.

Other fortification agates, with patterns resembling (and, at times, identical to) the badlands/grasslands Fairburns, had been found in and near limestone deposits in the Black Hills, but were thought not to be directly related to the Fairburn agates of the badlands and grasslands. These agates in the Black Hills had been given separate identities and were named for their locations, such as Tepee Canyon and Custer State Park.

An examination of the geologic history of the Black Hills, and correlation of the origin of the Chamberlain Pass Formation with the erosion of the Minnelusa Formation during the uplift, demonstrated the geological relationship and pointed to the Minnelusa Formation as the likely host formation of the Fairburn agate. The fieldwork that followed has verified the geologic relationship and established the host formation of the Fairburn as the Minnelusa limestone.

Significant amounts of sand, nodular chert and other silicified materials had accumulated in the Chamberlain Pass Formation. Subsequent erosion of the Chamberlain Pass Formation into the Cheyenne River (along the east side of Black Hills) concentrated sufficient volumes of gravel to be the basis for commercial gravel operations within which Fairburns are found. The very small number of Fairburn agates, compared to other components (unbanded chert, etc.), in the gravel deposits leads to the conclusion that during formation only a small fraction of a percentage of the nodular chert was subject to conditions favorable to the genesis of banded agates.

The part of the Minnelusa Formation containing the nodules of agate is dense, without voids or pockets, and consists of varying layers of limestone with variations consistent with changing surface conditions over millions of years. While chert nodules are present in a number of layers, banded nodules are present only in limited amounts and small concentrations, usually measured in feet. The largest known deposit, at Tepee Canyon, is estimated to be about one half mile in diameter and had sufficient concentrations of banded nodules to be commercially mined. Some of the smaller deposits which have been excavated have exhibited a high percentage of banded nodules, with as many as 80% of the nodules showing all or part fortification banding. When found in situ the nodules are found in layers horizontally following and consistent with the limestone bedding planes. Sediments are found to be draped over the nodules, indicating silica accumulation or silicification during lithification and prior to compaction.

Marine fossils are present in the Minnelusa and there are numerous examples of fortification agates either within or in association with such fossils. One of the predominant silicified fossils exhibiting inclusions of banded agate is *Chaetetes Mallepuracedus*. This fossil resembles coral and became extinct at the end of the Permian Period, which is also the time when the most recent accumulations of the Minnelusa were taking place. While the physical evidence observed indicates that the age of the agate should be consistent with the Minnelusa, there has been no additional research to confirm that observation.

Volcanic vs. Limestone Sedimentary Environment

During the past 25 years, thousands of Fairburns and other varieties of agate have been examined for structural characteristics visible to the naked eye or up to 10x magnification. Comparing

sedimentary-host agates such as Fairburns to volcanic-host agates has revealed a number of differences. As an example, when compared to Lake Superior agates, Fairburns do not exhibit the following characteristics or structures: 1) eyes, 2) tubes, 3) water level banding (also called Uruguay structure) 4) crystal impressions, 5) crystal replacements or pseudomorphs, 6) sagenite, 7) mineral inclusions, other than trace minerals causing color.

The absence of some of the above characteristics may be explained by the fact that the Fairburn appears not to have been formed in a preexisting void or cavity. The existence of the preexisting cavity would provide a place for the development of minerals or crystals within the cavity before the silica accumulation necessary for the development of the agate. At the present time there is no explanation for the lack of the other features other than the fact that the geologic environments of the host are radically different.

Significance of Spherulitic Crystallization in Fairburns

Particular attention is called to the role of spherulitic crystallization in the genesis of Fairburn agates. A significant number of Fairburn agates occupy only part, rather than all, of the nodule in which they are formed. The remainder of the nodule can be a gray or brown colored chert (silica-replaced limestone) or colored, but unbanded quartz, or both chert and quartz. The spherulites develop at seemingly random locations in the nodule, but are sufficiently organized so that the spherulites outline an area within the nodule of variable size. The spherulitic growth or radiation of fibrous quartz occurs only in a direction toward the center of the outlined area within which the banding develops. The remainder of the nodule appears to be unaffected by the spherulitic crystallization. In addition, separate areas outlined by the spherulites can develop banded agates of completely different colors and pattern within the same nodule. Whether the nodule is fully or partly banded, the development of spherulitic crystals appears to be the precipitating event. There is no apparent evidence of a preceding mineral or structure or cavity lining such as the celadonite cavity lining in certain Mexican agates (Cross).

Fairburns are known to exhibit clear macroquartz crystal bands, where the quartz crystals are visible to the naked eye. The quartz crystal growth is maintained in the same orientation toward the center of the agate, regardless of the size of the crystals.

A proposal for a theory of Fairburn agate genesis

The evidence gathered through observation and research indicates that the origin of the banded agate would be consistent with formation in a silica gel or viscous colloidal solution (Landmesser, Pabian) through spherulitic crystallization (**Diagram #1**). The accumulation of the amorphous silica in marine sediments would also appear to be consistent with Landmesser's silica sink accumulation through pore fluids (**Diagram #2**). This, in turn, would be consistent with the proposal by Knauth for the genesis of nodular chert (**Diagram #3**). Because Fairburn banding and color are always variable from nodule to nodule and even within the same nodule, the precipitating event or catalyst for banding would be from an internal chemical or electrical rhythm or stimulus.

Questions unresolved:

- 1) What is the source of the silica, biogenic or meteoric?
- 2) What are the conditions necessary for the development of spherulitic crystallization?

- 3) How the spherulitic crystallization is able to dictate the orientation of the quartz crystal and banding?
- 4) How and when trace minerals are transported into the nodule?
- 5) What is the cause of the precipitation of trace minerals into bands?
- 6) How do the same mineral oxides (i.e. red, yellow, black and red again) alternate within the same agate?
- 7) What is the age of the agate in relation to the host formation?
- 8) How long is the period of maturation (amorphous silica to fibrous quartz)?
- 9) What is the mechanism that creates deformation channels?

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Diagram #1



The nucleation of spherulite crystals begin to form at outer edge of area that will be banded

Diagram #2

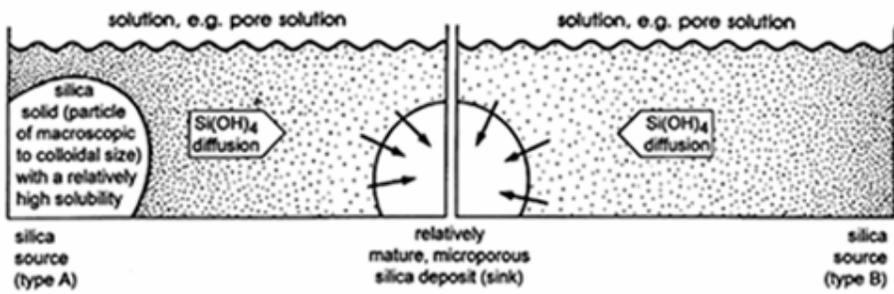
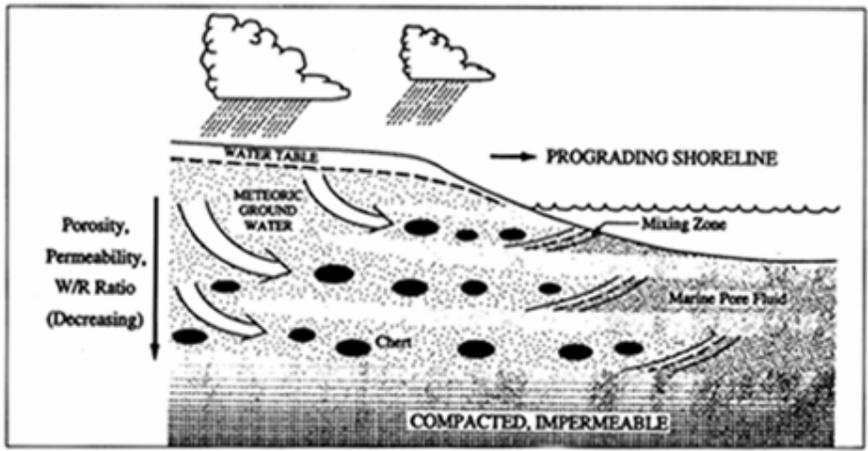


Diagram #3



Possible diagenetic setting of nodular chert formation

An American View of Scottish Agates

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How did a person from the New Mexico southwest get interested in Scottish agates?

I had been a subscriber to a UK publication, GEMS for many years. I had always been interested in minerals and fossils from around the world. GEMS always had a diverse subject matter that appealed to all collectors. I always read with interest the articles titled, "In the Footsteps of Heddle." (More on that gentleman, later). In a 1979 issue of GEMS was an advertisement, "Accommodation---Lapidary Landlady offers collecting holidays and field trips in Midland Valley of Scotland, looking for agates, rock crystal and minerals, visiting rock shops and talking rocks and lapidary. Bed, breakfast and evening meal (3 course). SASE please to Mrs. B.M. Houghton, 16 Wharry Road, Alva, Clackmannanshire, Scotland."

This program is dedicated to the memory of Margaret and Alan Houghton and to my mother, Mable Wheeler who started me in the mineral hobby.

To appreciate Scottish Pebbles as they are affectionately called, one should first visit the Royal Scottish Museum, Chambers Street, Edinburgh. I am sure our keynote speaker would agree with that statement. Here one sees cut and uncut agates collected by Heddle along with minerals arranged by districts in Scotland. Through the ears and eyes of Margaret Houghton we did our collecting first before we went to the museum.

Matthew Foster Heddle, like a few of us, started out in something other than mineralogy. He was a physician in Edinburgh in the late 1860's. He became Professor of Chemistry at St. Andrews University. His interest in minerals started in Edinburgh and lasted a lifetime taking him to the corners of Scotland recording mineral finds. Heddle completed a book, "The Mineralogy of Scotland." It was first published in 1901 and reprinted in 1923. It is considered to be one of the most complete records of Scottish minerals ever compiled. Starting in the March/April 1975 issue of GEMS and continuing for a number of months were these articles, "In the Footsteps of Heddle." Localities were described with such accuracy that with most maps, localities could be found.

Margaret Houghton was self taught in mineralogy and she had even taught some night courses in and lapidary at a local college. She was very aware of many locations and was always seeking new ones. As a result of my trip in 1980, I wrote an article for Lapidary Journal. A Professor of Geology in Glasgow saw Margaret's address, contacted her and gave her additional locations. That is called Networking!! Margaret and her husband, Alan, graciously shared this knowledge, knew landowners who would allow us to collect on their property and in event we weren't happy with what we found could go through their "chuckie" pile in their back yard.

To understand Scottish agates requires some research. Alas most mineral books by unnamed American authors did not mention Scotland but they all gave U.S. and South America for locations. To hunt for Scottish agates one needs to know how they were formed and where was the formation. Research in listed references talked about the old Red Sandstone period (over 300 million years ago). Large masses of lava, coastal and inland, flowed over an area which includes Kintyre, Arran and Ayrshire. The agates were formed within gas pockets and erosion from wind, rain, and wave action of the sea helps release them on the beaches for the collector to find. In the vesicles were also large nodules of celadonite (iron, magnesium, potassium silicate) and saponite (a hydrous silicate of magnesium and aluminum).

Agates still found in profusion (personal correspondence with Renato Forno, Leven, Fife, Scotland) include agates composed of purple amethyst enclosing cream-colored calcite, jasp agate, carnelian agate, agates with chalcedony enclosing green celadonite, onyx agate and the list goes on. All different colors can be found. Sizes range from pea size to nodules 4 to 5 inches in diameter.

In a letter from Margaret Houghton to myself in 1982 she described one agate hunting trip. (This was a trip to Macriinish Bay near Campbeltown). "As we parked facing the Atlantic, the rollers started coming in. We spent all day there dodging the waves, not a cloud in the sky, and the agates came up thick and fast. We had to force ourselves to sit down and drink tea! It was so exciting but also getting dangerous because the slope of the beach was acute and the tide was coming in fast, but we couldn't stop looking. Alan took a load back to the car and brought some more bags. The stones were getting larger all the time with the tide washing high on the beach. Maybe all the stones we collected that day aren't true agates but the colors of red, brown, yellow, green, white, mauve, etc. were terrific. (They had taken us to that collecting area in 1980).

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Structures and Micro-Structures in Scottish Agates

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The structures examined are faulting and displacement structures, segregation structures, stalactites and tubes of escape.

Faulting, attributed to tectonic movements, can be seen in some agates as the brittle fracturing of apparently solidified agate. In these cases the bands show a clean, sharp displacement. However, more rarely the bands are deformed, showing rolled edges that curve both up and down on either side of the displacement (Fig. 1). This implies a degree of plasticity and ductile fracturing, the inference being that when the bands were formed they were not completely solidified. Similarly detached bands that show displacement from their apparent initial alignment infer a degree of plasticity (Fig. 2).

Discoids or three dimensional ovoids can be observed in many agates (Fig. 3). These have been identified by others as cachalong, a mixture of opal and chalcedony, and this too can be inferred from the apparent lower hardness seen by undercutting on polished faces. These features are variable and are attributed to segregation of opal within a growing crystallizing chalcedony front. In onyx-banded agate the relationship between the segregation and the chalcedony is somewhat different. Here it has a flocculent appearance which on magnification appears to comprise of aggregated colloids. Coloured segregations that are not a silica phase show concentric zoning.

Stalactites are variable. Some show a distinctly gravity-related appearance without a foreign nucleus whilst others clearly show a celadonite or zeolite core around which chalcedony has grown. There are also chemically precipitated irregular stalactitic features which may be so close together so as to form a moss-like structure around which chalcedony deposits. Bending of stalactites in some agates has been cited as evidence of a flow direction.

The nature of the so called 'tubes of escape' still remains an enigma. This structure has been deemed by others to be central to understanding agate formation. The thinning of chalcedony bands in the tubes towards the outer surface of the agate has been cited by others as proof of movement of fluids both in and out of the agate; in contrast, Macpherson attributes 'tubes' to the dynamic forces of crystallization within a gel resulting in an increased volume that squeezes excess gel out of the cavity confines.

Figure 1.
Deformed bands showing rolled edges



Figure 2.
Detached features

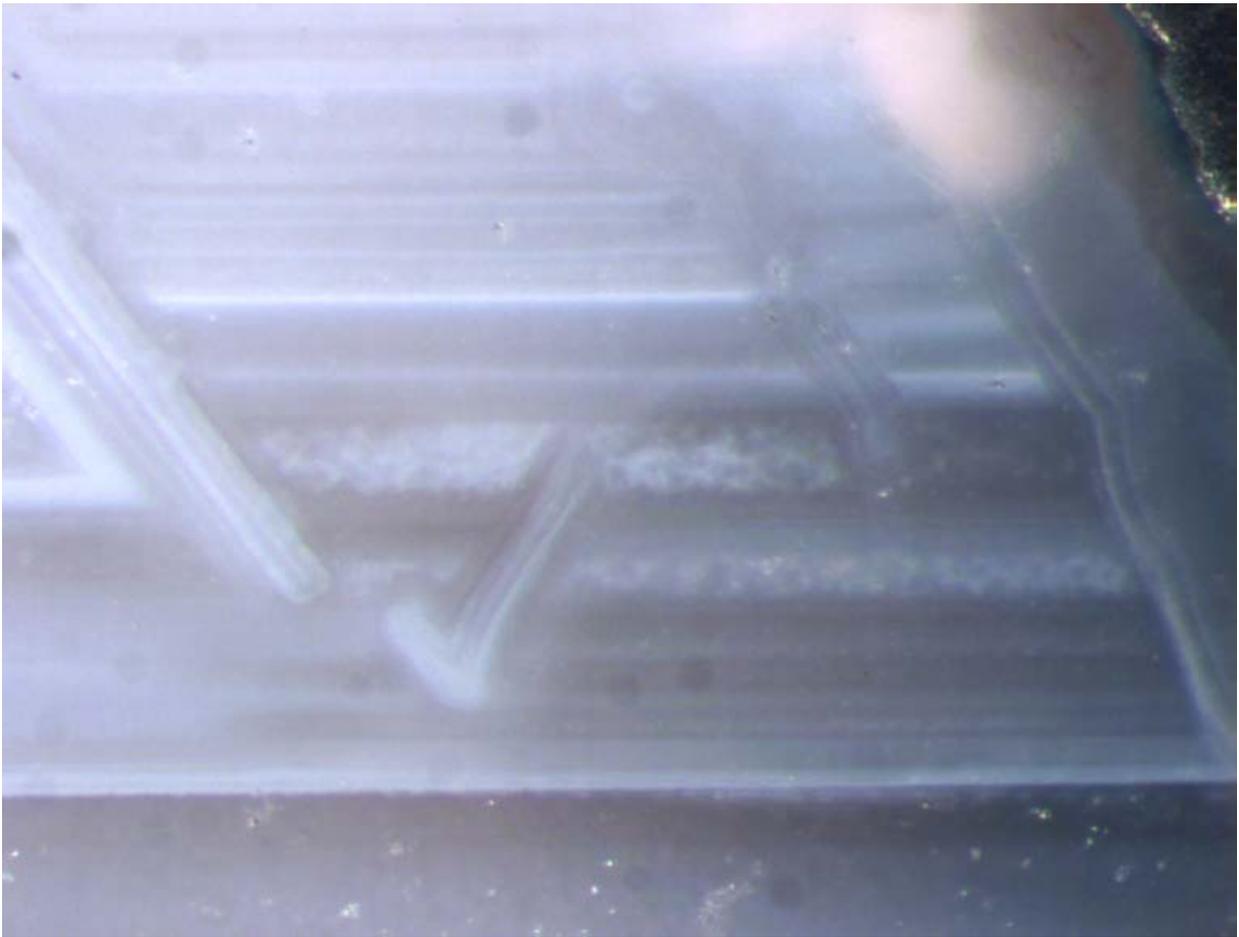


Figure 3.
Discoids or three dimensional ovoids observed in agates

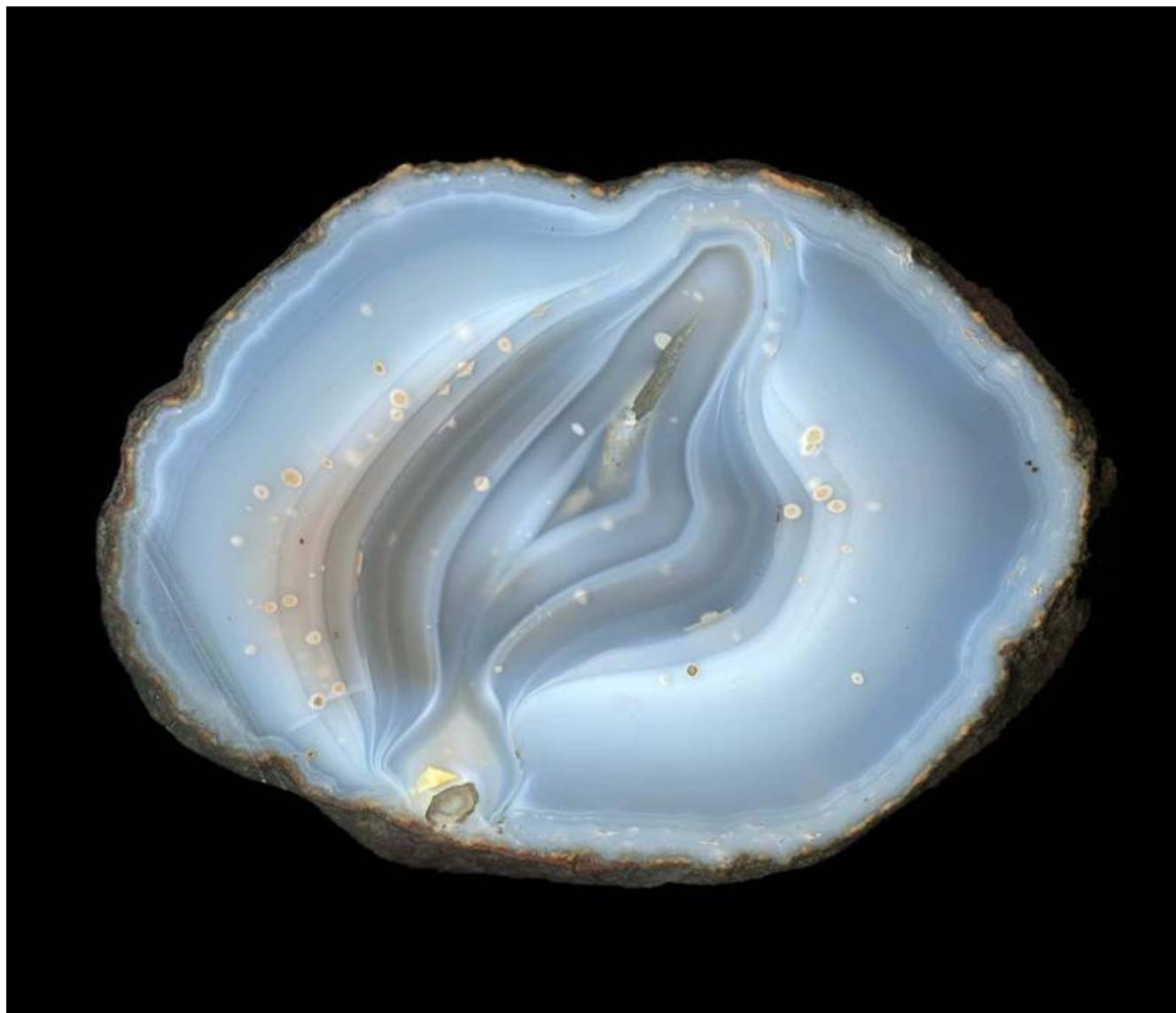


Figure 4.
Gravity controlled stalactites in agate

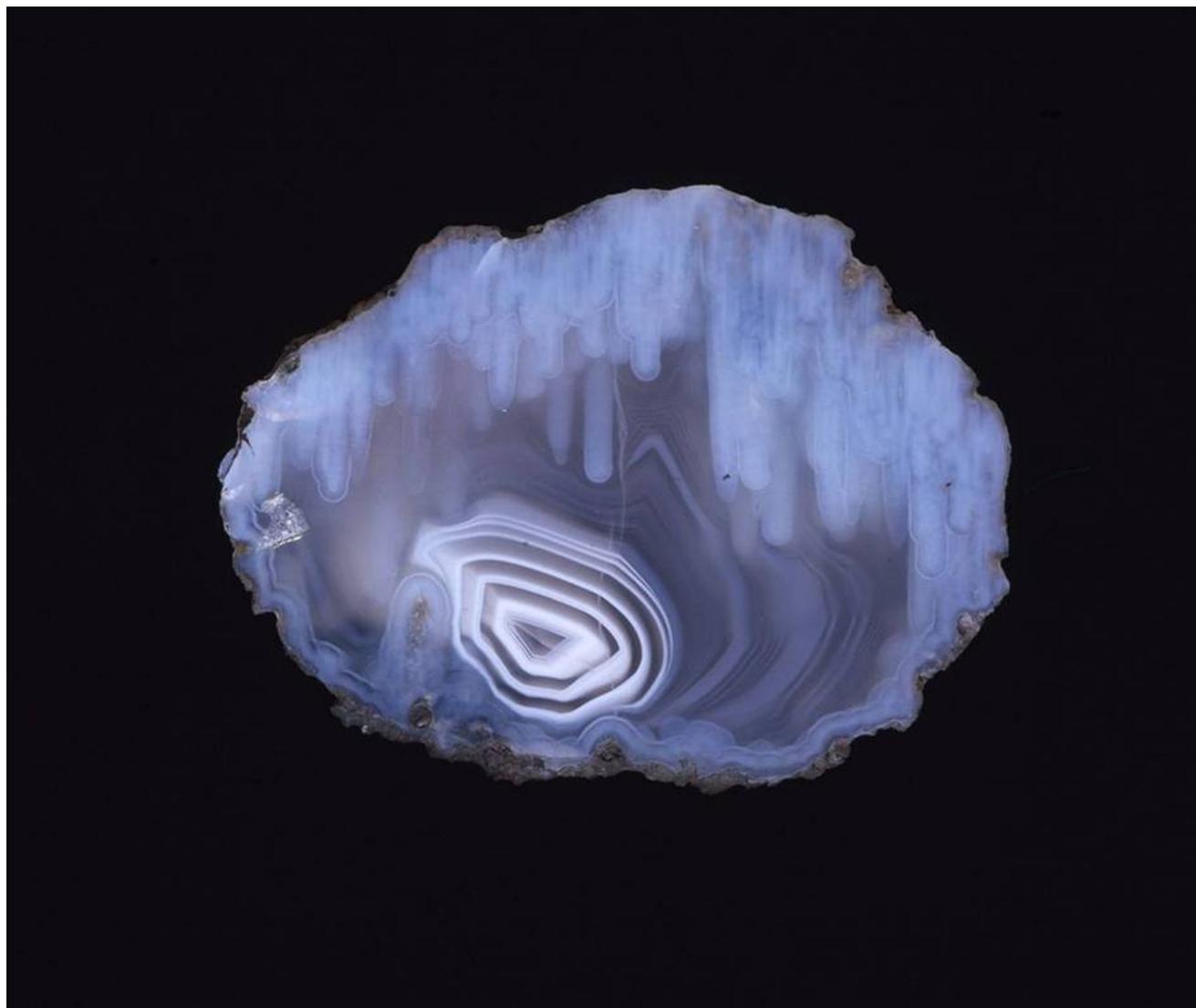
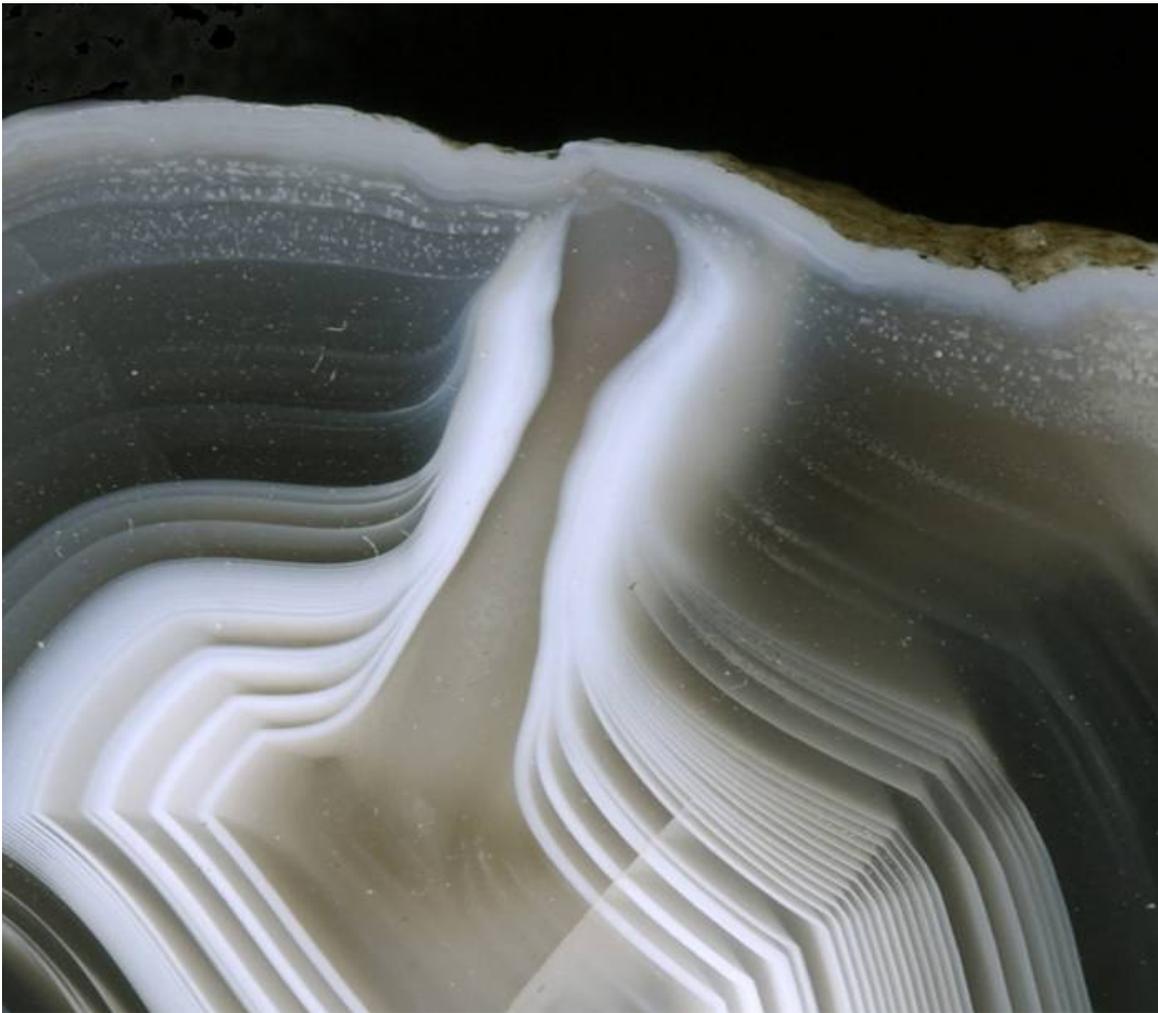


Figure 5.
Tube of escape showing band thinning



Silicification of Fossil Wood

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The formation of silicified wood preserving detailed cellular histology was once considered a molecule-by-molecule replacement of carbon by silicon, but investigators during the past 30 years have discovered that this form of petrification is considerably more involved. Today, this process is thought to be a product of initial supramolecular templating of polymerized silicic acid molecules via hydrogen bonding to available polysaccharides in woody tissue. This templating process is followed by additional silica emplacement, the subsequent transformation of these compounds into amorphous materials, and eventually to stable crystalline phases.

Leo and Barghoorn, in their landmark paper of 1976, *Silicification of Wood*, in *Botanical Museum Leaflets*, Harvard University, v. 25, no. 1., proposed the first detailed mechanism for templating and validated some of their ideas by replicating the initial stages of wood silicification in the laboratory. Silica derived from devitrification of tuffs or other sources produces monosilicic acid in ground water, which can eventually polymerize into higher molecular-weight species. These large molecules, containing copious numbers of hydroxyl bonding sites, can easily penetrate even small vascular tissue in plants. They orient themselves to form hydrogen bonds with the polysaccharides and other large carbon-based molecules that compose cellulose and lignin in the plant. This process is termed templating, and a silica lithomorph is produced. As the remaining original carbon tissue continues to degrade, additional hydroxyl sites become available for templating by polymerized silica.

At this point, the silicified wood does not resemble the hard durable material that collectors favor. Additional silica must be added to fortify the antecedent wood by a combination of deposition over the initially emplaced silica and by permineralization or addition of silica in remaining voids. Later, the templated silica loses hydroxyl ions and begins to form amorphous opal. The process by which silica forms solid compounds and converts to materials of increasing internal organization is generally given as:

Silicic Acid → Polymerized Silicic Acid → Opal-A (amorphous) → Opal-CT (cristobalite tridymite) → Microcrystalline Fibrous Quartz (Chalcedony) or Microcrystalline Granular Quartz (chert or flint).

After sufficient emplacement and permineralization of silica in the form of opal-A or opal-CT, a detailed representation of the woody structure can be produced. Some of the finest examples of preserved woody structure are observed during this phase of silicification. Subsequently, the opal loses water and begins to crystallize into chalcedony. Crystallization is usually a gradual process, and silicified wood often consists of both opal and chalcedony. Petrified wood specimens that have achieved this stage of silicification adorn fossil wood collections around the world. As the crystallization process continues, plant histological details may be lost. However, many wood

specimens composed purely of chalcedony offer examples of beautifully preserved cellular textures. The formation of chalcedony may continue until original woody textural details become blurred and eventually are lost.

Examples of advanced silicification begin to resemble limb casts and have poorly defined internal morphologies. The last obvious woody textures to vanish are the original growth rings, which may at this point be confused with agate banding. Figure 1 shows vestiges of cellular structures that have been obliterated and replaced by blobby-to-lacy textures in the chalcedony. Chalcedony is common in fossil wood, but less organized microcrystalline granular chert or flint may also result from continued crystallization. This material is organized less elegantly than chalcedony but results in a hard material suitable for lapidary purposes.

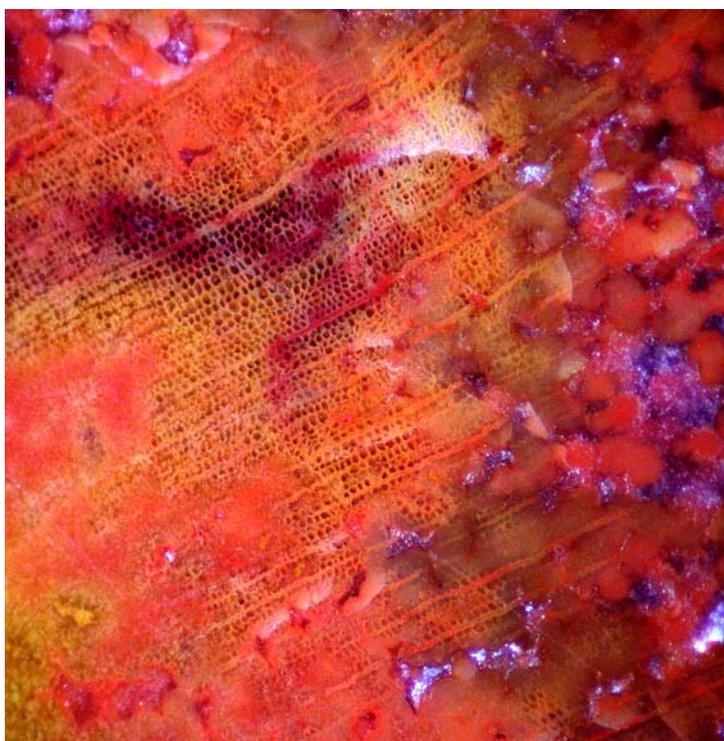


Figure 1. Cellular structure converts to blobby-to-lacy textures in Triassic silicified wood from Henry Mountains area, Utah. Width of view approximately 4 mm. (© Daniels 2005)

Figures 2 and 3 show silicification examples found in what are considered limb casts, but the textures are unusual and may have an organic origin. Figure 2 shows the “rods and cones” texture present in a number of petrified wood specimens commonly known as “red wood” from the Moab, Utah, area. The rods radiate away from the center of the limb, and the cones, which are centered on the rods, are concaved inward. Agates containing this unusual texture have not been observed by the author. Figure 3 shows small “threads” of a red hematitic-looking material floating in a translucent agate limb cast, also from a red wood locality near Moab, Utah. The origin of these features is unknown, but they resemble some form of organic material. Daniels and Dayvault (*Fossil Wood: A Closer Look at Ancient Forests*, in press) provide a more detailed

description of wood silicification and numerous photographs depicting various stages of this process.



Figure 2. "Rods and cones" texture in Jurassic red wood; specimen from Moab, Utah.

Width of view approximately 3 mm. (© Daniels 2005)

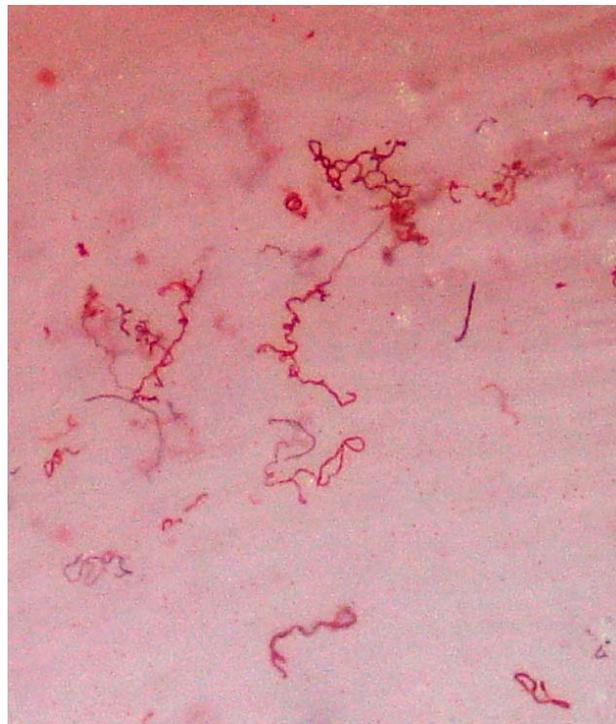


Figure 3. Small "threads" floating in translucent agate in a Jurassic limb cast from Moab, Utah.

Longest strand approximately 0.2 mm. (© Daniels 2005)

Fluorescence of Cryptocrystalline Quartz and Opal

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A distinctive feature of much agate and chalcedony is its characteristic green or yellow-green fluorescence under short-wave ultraviolet light. The intensity of the fluorescence is variable between localities and between samples from a given locality. Even in zones and growth bands within a single specimen, the fluorescence can vary from strong, to weak, to not discernable. This green fluorescence is known to be caused by the presence of uranium, in the form of hexavalent uranium as the uranyl molecular ion, UO_2^{2+} .

More specifically, the green fluorescence of uranium-bearing silica is due to adsorbed, hydrated uranyl ions, for which a formula can be written $(\text{UO}_2 \cdot n\text{H}_2\text{O})^{2+}$ (see Gorobets and Portnov, 1973; Gorobets and others, 1977). Uranium is present in sufficient concentration, and in the needed, hydrated environment, in those forms of silica which have a poorly organized crystal structure and which contain water as an impurity. Thus, well-crystallized quartz is rarely fluorescent, but the cryptocrystalline varieties and opal often are, because their poor crystallinity and greater surface area accommodate adsorbed molecules or ions on grain boundaries.

The green, uranyl-activated fluorescence has a distinctive spectrum, composed of a number of peaks within the green to orange portion of the visible spectrum, between wavelengths of approximately 500 to 600 nanometers (nm). This fluorescence is quite strong under illumination with short-wave ultraviolet light (approximately 254 nm, in the range known as UV-C) but only very weak under long-wave ultraviolet illumination (UV-A, approximately 360 nm). Fluorescence caused by the uranyl ion is accompanied by no visible phosphorescence (afterglow), whereas this may be observed in some other examples of mineral fluorescence, such as the common green fluorescence and phosphorescence of Mn^{2+} -activated willemite.

Fluorescence in well crystallized quartz, is often due to included minerals or in some cases hydrocarbons. Cryptocrystalline quartz from many localities may also fluoresce other colors that are usually not nearly as bright as the green uranyl fluorescence. Such fluorescence, most typically in whitish or yellowish shades, is most often seen in cloudy or opaque varieties, and often on chalky, weathered surface rinds. The Henkel Glossary of Fluorescent Minerals (Verbeek and Modreski, 1989), a compilation of colors of fluorescence seen in an exhaustive survey of minerals reported in the literature and personally observed by Dr. Gerhard Henkel, contains about two pages of entries for different varieties of quartz; reported colors of fluorescence in approximate order of frequency include green, white, cream, yellow, blue-white, tan, orange, pink, gray, brown, etc.

Many studies have been made of the cathodoluminescence (CL) of quartz, a technique which uses high-voltage electron bombardment, a more energetic type of excitation than ultraviolet light. Overall, quartz has relatively weak CL compared to many other minerals, and the green

fluorescence due to uranyl ions is not reported under CL. Marshall (1988) summarizes what is known of quartz CL, and reports colors including blue, dull red, violet, brown, gray, and others. Marshall's book only mentions one report of CL of chalcedony, deep purple.

Precious opal (opal with fire, or play of colors) is usually not fluorescent, or it may fluoresce white. However, much translucent to opaque, "common" opal (also sometimes known as "opalite" or "semi-opal") may fluoresce green due to uranyl ions, or other (often whitish), shades of color. The clear, glassy variety of opal known as hyalite is particularly likely to contain enough uranium to give it a bright-green fluorescence. A number of other minerals, especially those of low-temperature, secondary origin, may appear macroscopically to fluoresce green, when the fluorescence in fact is often due to thin coatings of clear hyalite opal; the author has observed this on calcite, aragonite, and analcime. The Henkel Glossary notes only a few reports (as white or purple) of the fluorescence of precious opal, but many of common or hyalite opal fluorescing green, yellow-green, cream, white, blue-white, blue-violet, and other shades. The cause of the fluorescence in all the colors, other than green, observed in quartz varieties and opal, remains basically unknown or little studied. A compilation of spectra by Gorobets and Rogojine (2002) gives a number of luminescence spectra of different varieties of quartz and suggestions as to their causes, many of which involve lattice defects and vacancies.

Figure 1 (taken from Newsome and Modreski, 1981) compares UV-excited fluorescence emission spectra of common opal (Virgin Valley, Nevada) and meta-autunite, a hydrous uranyl phosphate mineral. The spectra are similar, each showing the distinctive "fingerprint" of peaks due to the quantized vibrational modes of the triatomic UO_2^{2+} ion (picture three atoms joined together by springs), but in the spectra of opal, the peaks are less distinct. The same broad, less well-resolved, spectrum is seen for chalcedony and its varieties. Spectra of some other uranium minerals and uranyl-containing silica minerals can be seen on the web page of Noda and Kinnin (2004).

Relatively few published studies give actual analyses of the uranium content of fluorescent chalcedony or opal. Staatz and Bauer (1951) reported between 0.002 to 0.012 wt. % (= 20 to 120 ppm) uranium in opal layers from Virgin Valley, Nevada. Zielinski (1982) reported between 6 to 823 ppm U in Virgin Valley opal; values in one of the purest opal layers ranged from 10 to 242 ppm, with a mean value of 91 ppm. Zielinski (1980) reported approximately 60 to 240 ppm uranium in silica (chalcedony) noted as being fluorescent yellow-green, associated with uranium deposits in the White River Formation (Oligocene), Shirley Basin, Carbon County, Wyoming; other cryptocrystalline silica layers in the formation contained between 10 to 142 ppm U. Zielinski reported silicified wood (presumably nonfluorescent) from the Wind River Formation, Carbon County, Wyoming, to contain 5 to 10 ppm U. Gray chert (presumably nonfluorescent) in the Madison Limestone (Mississippian), Albany County, Wyoming, contained about 2 ppm U, but blue-white cryptocrystalline silica veinlets in that formation contained 20 to 142 ppm U. Zielinski (2005, in this volume) further describes the Virgin Valley occurrence.

Additional data on uranium content of fluorescent opal and chalcedony were given by deNeufville and others (1981). They reported:

Spruce Pine, NC, glassy hyalite opal, 3000 ppm U (along with 5000 ppm Cu)

Spruce Pine, NC, milky hyalite opal, 58 ppm U
 Virgin Valley, NV, opalite, 460 ppm;
 Scenic, SD, hyalite opal, 180 ppm U
 near Casper, WY, common opal, 63 ppm U
 Bad Rivers Mountains, AZ, opalite, 24 ppm U
 near Deming, NM, chalcedony geode, 18 ppm U
 Dugway, Utah, chalcedony concretion, 15 ppm U

Because different samples of the minerals from all these localities may vary considerably in their uranium content and brightness of their fluorescence, one cannot draw positive correlations between uranium content and fluorescence from a single analysis. For example, the chalcedony analyses cited above from Deming, NM and Dugway, UT are quite low in uranium, but some specimens from these same localities can have a very bright fluorescence; those probably have a considerably higher uranium content than the samples analyzed. deNeufville and others (1981) did report relative intensities of fluorescence brightness along with their analytical data. The last several samples listed above, with low uranium concentrations, had low relative brightness, 100 to 600 units on a scale in which the brightness of their sample of Virgin Valley opalite was 37,400, and the Spruce Pine glassy hyalite opal was 43,300.

Brightly fluorescent cryptocrystalline silica occurs at many different localities worldwide. “Youngite” is chalcedony in stalactitic forms, coated by a layer of drusy white quartz, found near Guernsey, Wyoming; the chalcedony often gives the overall material a variable, weak to very bright, green fluorescence. Slightly banded chalcedony (grayish-white to faint pink) lining the interiors of gas cavities in rhyolite lava in the Peloncillo Mountains near Geronimo Pass, Hidalgo County, New Mexico, often fluoresces bright green (Modreski, 1996). Also in southwestern New Mexico and adjacent Arizona, flattened “chalcedony rose” nodules which weather out of rhyolite lavas in the Mogollon-Datil volcanic province, are often brightly fluorescent (one is illustrated in figure 14 in Modreski, 1987). Translucent, gray chalcedony with black moss-like inclusions from Sweetwater County, Wyoming, known as “Sweetwater agate”, is well known for its strong green fluorescence.

Fluorescent hyalite opal is perhaps best known from Spruce Pine, North Carolina, where it occurs as thin, clear, brightly fluorescent coatings, also colored distinctly green in visible light due to their copper content, on fractures in granite and pegmatite. Brightly fluorescent, botryoidal globules of glassy hyalite opal are also known from Valeč, Bohemia, Czech Republic; Monok, Zempleni Mountains, Hungary; Cerro de Tepozan, San Luis Potosi, Mexico; and numerous other localities worldwide.

Publications that discuss and illustrate general aspects of mineral fluorescence, including that of silica minerals, include books by Robbins (1983, 1994); Warren and others, 1995; and the article by Modreski and Aumente-Modreski (1996).

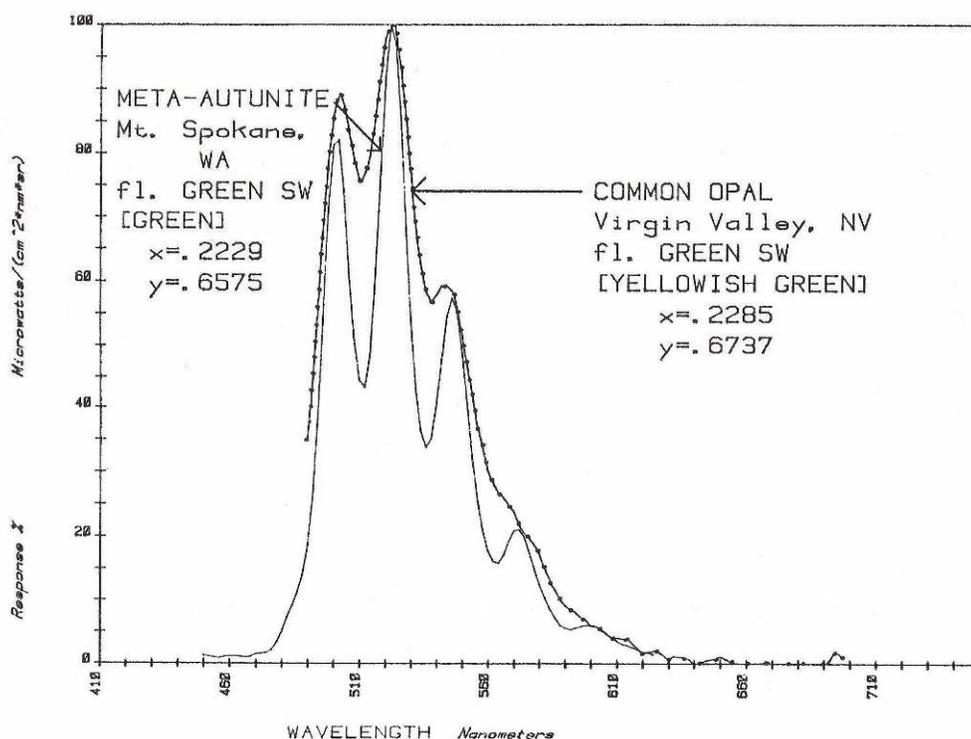


Figure 1. Fluorescence spectrum of common opal from Virgin Valley, Nevada, compared to that of a uranium mineral, meta-autunite. Taken from Figure 14 of Newsome and Modreski (1981).

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Uraniferous Opal, Virgin Valley, Nevada, Contains Evidence of its Age and Origin

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The Virgin Valley in Humboldt County, northwestern Nevada is a well-known source of gem-quality precious opal. Common opal is also relatively abundant in the valley, some of it displaying a bright yellow-green fluorescence when observed under short-wave ultraviolet light (Staatz and Bauer, 1951). The fluorescence is of particular interest to mineral collectors and is caused by trace impurities of uranium (U) present in the oxidized, U^{+6} valence state. The most highly fluorescent opals contain several hundred to more than one thousand parts-per-million (ppm) U, and are pale-green in color, translucent, and have a distinctive conchoidal fracture. Highly fluorescent opal is found in prospects located on the east side of the valley, typically in discontinuous pods and lenses as much as 0.7 m thick (Staatz and Bauer, 1951). The opal can be found by walking along the strike of a distinctive host “chalk-white ash bed” within the upper Virgin Valley Formation (Merriam, 1907).

The host Virgin Valley Formation consists of at least 300 m of tuffaceous sedimentary rock with associated ash-fall layers, and volcanoclastic debris derived from older silicic volcanic rocks (Wendell, 1970; Brophy, 1980). The formation was initially deposited in a fluvial/lacustrine setting, with the majority of the sediments deposited under lacustrine conditions. Deposition was confined to a structural depression that may have been a volcanic caldera (Henry, 1978). The upper lacustrine facies of the Virgin Valley Formation was deposited in Miocene time based on reported ages of volcanic ash layers of 14.4 ± 0.8 and 13.9 ± 2.0 million years (Zielinski, 1982). Major structural features in the area of Virgin Valley include north-south-trending folds of Miocene to Pliocene age. Other features are Miocene and younger, dominantly northwest-trending normal faults that formed and were periodically reactivated in response to regional Basin and Range tectonism (Cathrall et al., 1978).

In addition to their appeal as fluorescent minerals, the U-bearing opals of Virgin Valley first attracted attention in the 1950's as possible prospecting guides to undiscovered economic concentrations of U. Staatz and Bauer (1951) reported the U mineral carnotite as a fracture coating or a fine layering within some opal. Since 1950 more than 700 U claims have been located in the Virgin Valley area, most in the Virgin Valley Formation at the south end of the valley. The U.S. Geological Survey began a study in 1980 to determine the age of the U-rich opal and the conditions of its formation. The results of that study (Zielinski, 1982) are summarized below and illustrate the types of information that can be obtained from scientific investigation of U-rich opal.

Initial sampling of U-rich opal from the east side of Virgin Valley revealed that the host “chalk-white ash bed” was actually a diatomite bed (Zielinski, 1982). Paleontologic study of the diatoms indicated types that were most likely deposited in a shallow lake of low salinity and near-neutral pH (Zielinski, 1982). Diatoms provided a source of nearly pure, fine-grained,

relatively soluble biogenic silica that could be dissolved and re-precipitated as a hydrous silica-gel precursor to opal. Diatomite from the site contains approximately 20 ppm of U, an amount that was probably incorporated in biogenic silica during original precipitation from the lake water. The average crustal abundance of U is approximately 2-3 ppm, so the diatomite acted as a natural pre-concentrator of U. Laboratory study of the uptake of U by freshly-precipitated silica gels indicated 400- to 1000-fold enrichment of U in the gels compared to U concentration in solution (Zielinski, 1980).

Inspection of polished sections of the fluorescent opal under high (750X) magnification confirmed the presence of relict circular structures that represented silica pseudomorphs of diatom structures (Zielinski, 1982). Some of these areas contained circular cavities of 10- to 15-micrometer diameter that contained two-phase (liquid + minor gas) fluid inclusions. The inclusions likely contained fluids trapped under the conditions of opal formation and their properties were studied using specialized microscopic techniques. Homogenization temperatures of 14 inclusions ranged from 100° to 250 °C and freezing-point depression measurements indicated a solution of low salinity. These observations indicated that diatomite dissolution and re-precipitation of silica gel occurred in relatively hot, dilute solutions and the process was probably driven by changes in temperature. Solutions containing dissolved silica were also sufficiently oxidizing to maintain dissolved U as an oxidized U^{+6} species.

The time of formation of U-rich opal was estimated by U-Pb dating (Zielinski, 1982), a technique that utilizes mass spectrometric measurements of U and lead (Pb) isotope abundances. The calculated age is based on the abundance of particular “radiogenic” lead isotopes (^{206}Pb and ^{207}Pb) that form at a known rate based on the radioactive decay of their U isotope parents ^{238}U and ^{235}U . A critical assumption for U-Pb dating is that the U-bearing host (opal) remains a chemically closed system with respect to U and all of its decay products (including Pb). The uniform U concentration (and also fluorescence) in individual fluorescent bands, and the preserved sharp contacts between bands of different fluorescence intensity provided evidence for immobility of U (Fig.1). The massive character of the in-place opal also encouraged an assumption of chemical closure. The abundance of Pb in the opal was <1 ppm and this low value indicated that a significant percentage of the Pb might be generated by in-situ decay of parent U. Corrections were made, however, for Pb isotopic contributions from the natural Pb present in the local environment. The abundances of parent U isotopes ^{238}U and ^{235}U , compared to their respective decay products ^{206}Pb and ^{207}Pb , provided two independent dates that could be measured simultaneously and checked for agreement. Another check on the procedure involved sampling the exterior and the interior of a large banded opal layer (sections D and A, Fig.1) to check for the expected relative-age progression. The resulting $^{238}\text{U}/^{206}\text{Pb}$ ages and $^{235}\text{U}/^{207}\text{Pb}$ ages ranged from 1.87 and 1.98 million years in the exterior to 2.54 and 2.40 million years in the interior.

The apparent 2 million-year age of opal formation is much younger than the approximate 14 million-year depositional age of the host Virgin Valley Formation, and the Miocene age of other silicic volcanic rocks that rim the Virgin Valley (Zielinski, 1982). Episodes of basaltic volcanism within northwest Nevada in Pliocene and early Pleistocene time may have provided

the impetus for more recent crustal warming. The hot water that facilitated dissolution of diatomite and formation of U-rich opal probably originated at depth and rose along a local high-angle normal fault. Where the fault intersected relatively permeable strata of the Virgin Valley Formation, the solutions were able to move laterally within the strata and react with mineral constituents. A similar mechanism may explain the formation of laterally extensive silicified ash beds on both sides of Virgin Valley. An observation in support of this model is the presence of a modern warm spring situated along a local fault within 1.5 km of the opal sampling location.

The fluid inclusion, chemical, and isotopic record preserved in U-rich fluorescent opal from Virgin Valley provides important information regarding the conditions and timing of its formation. Uraniferous opals from other localities have been dated by the U-Pb technique (Ludwig et al., 1980; Neymark et al., 2002) and by a U-series method (Paces et al., 2004) that measures ^{234}U and ^{230}Th decay products of ^{238}U . Uranium-bearing opals are thus becoming more highly recognized as sources of scientific information as well as mineralogical interest.

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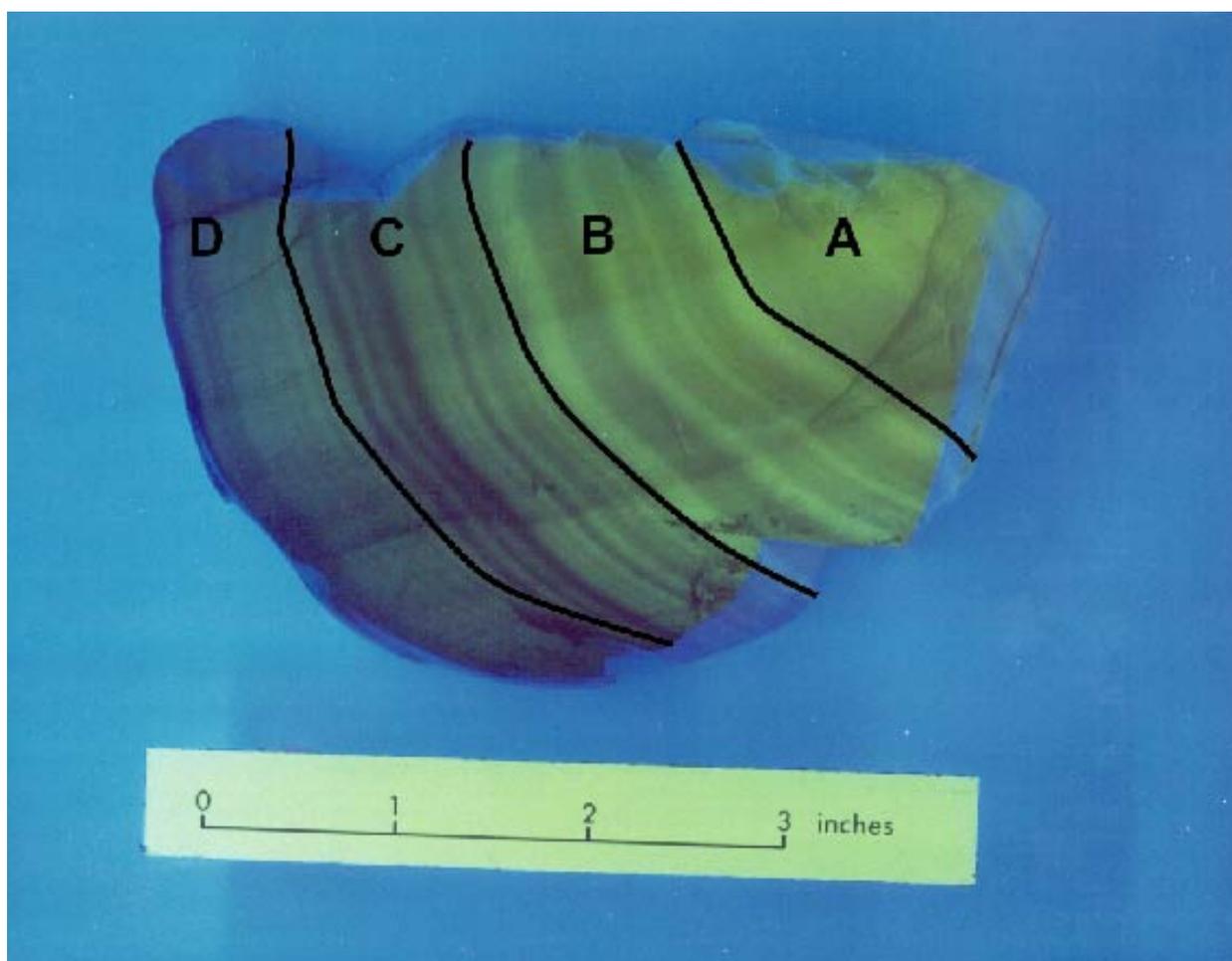


Fig.1. Photograph of uraniferous opal of the diatomite locality in Virgin Valley, northwestern Nevada, taken under ultraviolet light illumination. The four sections selected for dating are labeled A-D. Brighter bands of greater fluorescence have higher U content.

Basal (c) Face Quartz, its History and Occurrences

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As man became interested in minerals and curious about them he gathered and shared information. A major publication by Dr. Victor Goldschmidt, *Atlas der Krystallformen* (1917) depicted several occurrences of quartz crystals showing the basal or c face. Of the publications that Goldschmidt cited as sources of his information, I have only been able to locate one in the library of the Technische Universität Berlin, a paper by Maskelyne (1877). This paper describes five amethyst quartz crystals showing the c face. A detailed study of the faces on these crystals leads to the conclusion that they all are fourling twins. All were crystals showing no prism faces and suspected of occurring in a geode.

In *Les mineraux de la Belgique* (Buttgenbach, 1938), in the chapter on quartz, page 208, the author mentions that in the collection of the University of Liege there is a crystal terminated with the basal plane (0001). This is specimen number 11026 and is still in the collection. The specimen is from Nil-Saint-Vincent.

I have obtained four macro-size crystals showing the basal pinacoid: one amethyst from Bolivia, one amethyst from the Four Peaks mine in Arizona, one smoky crystal from Hidden, North Carolina, and one from the CF&I marble quarry near Monarch Pass, Colorado.

In the micromount collection of the Denver Museum of Nature & Science there are 14 quartz crystals showing the c face. Several occurred in rhyolites, several are from the Amethyst mine at Creede, Colorado, several are from the Olsen ranch, Park County, Montana, and several are from the Ellis Emerald mine, North Carolina. These crystals showing the basal face were popular with micromount collectors and most museums that have micromount collections will have some in their collections.



Micromount quartz crystal from Ruby Mountain, Colorado

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Phenomena in Agate: Clues to its Formation?

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Over the centuries there has been considerable interest in and appreciation of agates, and as knowledge, interest, and the number of localities known have grown, so have the number of theories about how agates have formed. It is only human to try to conjure possible explanations (a.k.a. theories) to explain events or phenomena. That is one part of the scientific method. The second and most important part of the scientific method is to test the theories. Agates present a problem for scientists who are mere mortals. Many lines of evidence and experience indicate that the actual processes used by nature to form agates require chunks of time that are not practical for laboratory duplication. Collection and knowledgeable observation of phenomena shown by agates offer a rewarding avenue for identifying and evaluating processes possibly involved in agate formation, and perhaps most importantly, eliminating some of the otherwise theoretically possible scenarios.

For our purposes we are using the term phenomena as it is defined in the *O.E.D.* (1971, 2152): "In scientific and general use: a thing that appears, or is perceived or observed; an individual fact, occurrence or change as perceived by any of the senses, or by the mind: applied chiefly to a fact or occurrence, the cause or explanation of which is in question." The various phenomena shown by agates are the basis for much their charm and fascination, and also are clues as to how agates have formed.

Careful examination of many different agates from disparate places can give science a sort of time-lapse picture of the agate-forming process. We have been attempting to enumerate and, and where possible, to classify observable phenomena in agates as part of the mundane task of trying to bring some measure of rational order to an almost ridiculously extensive collection of agates (and other SiO₂ minerals). We have seen large quartz (including agate) collections organized in many ways including by: aesthetics (the most common), location (at least it works), size (often dictated by available space), date of acquisition (this also works), color (fun but futile), name (this is becoming or has become the preponderant way for other mineral species, but for agate and other quartzes it is laughably futile), and of course, the ever popular random order.

As part of research on a book on quartz minerals we have made an attempt to visit, examine, and photograph the quartz portion(s) of as many as possible of the Western World's major museums and many private mineral collections that have significant quartz holdings. This effort, spread over the last 30 or so years has barely scratched the surface, but has shown us that the rational organization of quartz specimens in general, and agates in particular, is a conundrum that is not easily solved, but attempting to systemize them can be rewarding in many ways.

We have observed and enumerated 111 different phenomena shown by agates. Among a few of the most interesting and important are: concentric agate banding; the nature of bands as revealed by polarized light, microscopy, and SEM; horizontal (“Uruguay structure”) banding; *Einflusskanäle* (German =inflow channels, a term coined by Noggerath in 1849 and subsequently called “in flow” or “out flow” or escape channels and many other synonyms by other authors; Liesegang rings (yes, they are found in agates, but going perpendicular to the direction postulated by Dr. Liesegang); dendrites; moss structure; deformation of bands or layers in agate etc., etc.. We have attempted with varying degrees of success to fit the 111 specific phenomena that we have observed into 17 broad categories including:

- A. Host rock
- B. Chemistry of agate
- C. Mineralogy of agate
- D. Structure of agate
- E. Original plastic nature of proto-agate
- F. *Einflusskanäle*
- G. Sequence
- H. Uruguay structure
- I. Botryoidal to stalactitic structure
- J. Liesegang rings
- K. Colors and color distribution in agate
- L. *Entglasung*
- M. Iris agate
- N. Fire agate
- O. Pseudomorphs
- P. Specific types reflecting type of occurrence
- Q. Other (a very large category at this time)

We have no illusions about any degree of completeness. We confidently hope these categories will be significantly altered and expanded before this symposium is over. It is our hope that attempts to expand the list of observable phenomena and to better systemize their arrangement will throw additional light on the nature and origin of agates, as well as our appreciation of them.

Our Power Point presentation will illustrate some examples and some problems. In addition we will have a list available to those who are interested of the phenomena and how we have categorized them. Another copy will also be available to those who are willing to make corrections, additions, and/or suggestions.

We also will have some examples of some of the more difficult, intriguing, and enigmatic agates we have encountered.

The Blue Agate of Kittitas County, Central Washington

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“We have jewelry made from an agate found near here and found nowhere else in the United States, the blue agate, a true souvenir of this valley.”
 — J. N. O. Thomson, ca. 1941

Introduction. Blue-colored agate of central Washington State has been valued as a gemstone since the early 1900s and is claimed to be of fame in Germany, the Orient, Arab countries and all over the United States (Nuckles, 1984). Known as *Ellensburg blue*, after the central Washington township of that name and the deep blue color that specimens may possess, the agates are esteemed by townfolk as being unique in the USA (Clinesmith, 1936; Thomson, 1961).

Field occurrences and geology. Blue and grayish-blue colored agates are found in Kittitas County, central Washington. The county is bordered by the Cascade Mountains and the Columbia River and is dominated by the semi-arid to arid basaltic landscape of the Columbia River Basalts. Agates are associated with two separate formations. *In situ* occurrences are found in the altered Eocene Teanaway Basalt, a formation comprising basalt lava flows and pyroclastics, and minor rhyolitic ash-flow tuffs. *Ex situ* occurrences are associated with montmorillonite and hematite-cemented gravels comprising the Pliocene aged Thorp Gravel.

Mineralogy. Ellensburg blue and associated non-blue-colored agates occur as concentrically banded and non-banded specimens. Agates fill joints and void-space in pervasively altered Teanaway Basalt lava. These lavas have an alteration mineralogy of groundmass clays, and cavity calcite and SiO₂. At some localities calcite veins and void-fill dominate over SiO₂ and calcite is intergrown with SiO₂. *Ex situ* specimens range in weight from several grams to an extraordinary 6.4 kg (Nuckles, 1984) and are exclusively SiO₂ phases (sometimes with molds of calcite rhombs and cleavage).

Banded specimens comprise sub-millimeter to 0.5 cm-thick bands of chalcedony. Bands are macroscopically recognizable by color or hue variation and microscopically by grain-size changes or extinction characteristic variations. Commonly the inner surface of a banded specimen comprises a drusy surface of 1–2 mm-long subhedral–euhedral microcrystalline quartz. In some specimens this surface is thinly (1–2 mm) covered by a further layer of botryoidal chalcedony. Unbanded specimens are massive chalcedony. Few samples contain petrographically resolvable fluid-inclusions although minor opaque inclusions (hematite?) occur in localized patches at and near the rock-agate interface in some samples.

X-ray diffraction (XRD) analysis reveals the dominant presence of α -quartz (microscopically fibrous = chalcedony). Slightly increased chalcedony diffractogram backgrounds relative to quartz prepared in the same way, suggest the presence of minor amorphous silica. Moganite is detected in chalcedony samples (Figure 1). Volume proportions (as a percentage) of moganite and α -quartz in a given sample were estimated after the manner used by Moxon & Ríos (2004) on diffraction data ranging 18–23 °2 θ modeled with Pseudo Voigt functions and are found to range 6–13%. The occurrence of moganite is confirmed by micro-

Raman spectra and a prominent peak at $495\text{--}510\text{ cm}^{-1}$, the moganite band (Kingma & Hemley, 1994; Götze et al., 1998).

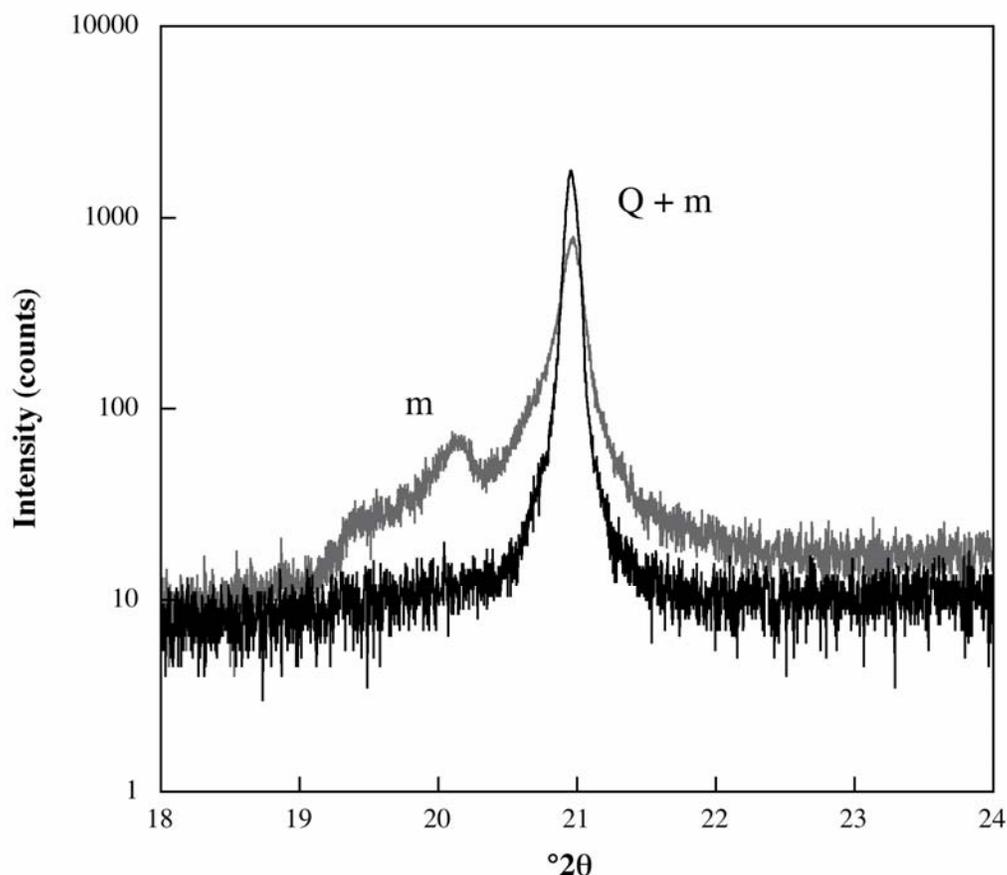


Figure 1. Uncorrected X-ray diffractograms of colorless and bluish bands in a single specimen of Ellensburg blue. Symbols relate peaks to mineralogy: “Q” is quartz, “m” is moganite. The colorless band of microcrystalline quartz (lower background, darker pattern) contains α -quartz only, and the bluish band of chalcedony (higher background, gray pattern) comprises α -quartz and moganite. The bluish band contains about 13% of moganite and probably some proportion of amorphous silica. Operating conditions: Cu $K\alpha_1$ radiation; 40 kV, 40 mA; 20 mm divergence and anti-scattering slits; $0.003^\circ 2\theta$ step size, 2 s per step, continuous scan mode.

Origin of blue-gray coloration. Prized samples of Ellensburg blue are often described as having a cornflower blue color (red-green-blue color space: 100r 149g 237b). Blue hues range, however, from grayish-blue (170r 210g 255b) to purplish-dark-blue (11r 22g 115b). Those samples accepted by local rock-hounds as “true blues” are those that exhibit a reddish-hue when held up to a bright light such as the Sun. Blue-colored bands are observed in agates worldwide including those from California, Nebraska, Brazil, Tibet, Romania, Taiwan, and Switzerland.

Blue coloration is common in nature (Nassau, 2001). Examples include ocean water, flower petals, and the human eye. Prum et al. (1994) show how the production of green and blue color in the skin of a bird is due to ordered hexagonal arrays of parallel collagen fibers that

diffract light as described by the Bragg equation. Zolensky et al. (1988) found that blue-colored quartz in the Llano rhyolite, Texas, was so colored as a result of light-scattering off 60 nm-sized (average) ilmenite inclusions. This contrasts with the rutile-bearing charnockitic blue quartz studied by Jayaraman (1938) which appears to be colored by light-scattering from 50–200 nm-sized “colloidal particle” inclusions. The mechanism of blue-coloration in chalcedony is assumed to be light-scattering (Moxon, 1991; Rossman, 1994) although until now this has been unsupported by direct observations.

Optical absorption spectra were collected from locations within a blue–colorless–grayish-blue banded Ellensburg blue sample. Spectra show continuously increasing absorption with wavenumber as is typical for light-scattering by sub-micrometer to micrometer-sized particles. Absorption bands of ions such as Cu^{2+} or a rare-earth element that may cause a blue color, are not detectable. This is consistent with electron microprobe analyses which do not detect trace-elements and cathodoluminescence (CL) spectra that only have broad emission bands at about 650 nm and 500 nm. The broad band at ~500 nm is often detected for amorphous silica (Götze et al., 2005; J. Götze, pers. comm., Feb. 2005). These results suggest that the blue-coloration is not compositional, but is related to light-scattering.

Scattering of polychromatic light to produce blue color occurs when the size of scattering particles are about one-tenth of the wavelength of visible light. Visible light has wavelengths ranging 390 nm (violet) to 760 nm (red). This is the phenomenon of Rayleigh scattering. A feature of this scattering is that higher frequency light (shorter wavelength) is scattered more than lower frequency light such that violet-blue light is scattered more than red light. Also, the intensity the scattered light varies inversely with the fourth power of the wavelength (this is the Rayleigh law). This means, for example, that scattering due to incident violet light (400 nm) is 4.42 times more intense than scattering due to incident yellow light (580 nm). Rayleigh scattering is the mechanism that produces a blue sky.

To identify particles that might Rayleigh scatter in Ellensburg blue, freshly broken surfaces of macroscopically colorless and grayish-blue chalcedony bands from a single specimen were imaged by high-resolution scanning electron microscopy (SEM). In both samples, bundles of fibrous chalcedony predominate. Imaged only in the colored band are disseminated spheroids with diameters ranging 34–172 nm (Figure 2). Thirty-five percent of the spheroids have diameters less than or equal to one-tenth the wavelength of light. These spheroids are likely to be the particles responsible for Rayleigh scatter in blue-hued bands.

The exact nature of the spheroids is uncertain. Compositionally they are likely to be silica given the absence of other elements in compositional analyses. Texturally, they are reminiscent of the more-or-less ordered spheres of opal although much smaller. Gem-quality Australian opal has sphere diameters of about 250 nm, larger than the Rayleigh limit. The spheroids appear to be non-crystalline (Figure 2) and this is consistent with inferences on the presence of amorphous silica from XRD diffractograms and the ~500 nm broad-band emission in CL spectra.

Comparison with other colored agates. The occurrence of 40–80 nm-sized particles in other cryptocrystalline quartz samples was investigated. A sample of bluish vein chalcedony from Switzerland and a sample of colorless-and-white banded agate from Idar-Oberstein, Germany, were investigated by SEM. As for Ellensburg blue samples, the Swiss chalcedony contains spheroids that are likely responsible for Rayleigh scattering and blue coloration. No spheroids were observed in the Idar-Oberstein sample. However, macroscopically white-colored bands comprise linear bands of approximately micrometer-sized cavities, which

petrographically, are single and double-phase fluid-inclusions. These inclusions are on the order of the wavelength of visible light and give rise to another light-scattering phenomenon, Mie scattering. The color of Mie scattered light is white because all incident wavelengths are scattered. Macroscopically, a reddish-hue is not observed for the Idar-Oberstein sample when held up to a bright light.

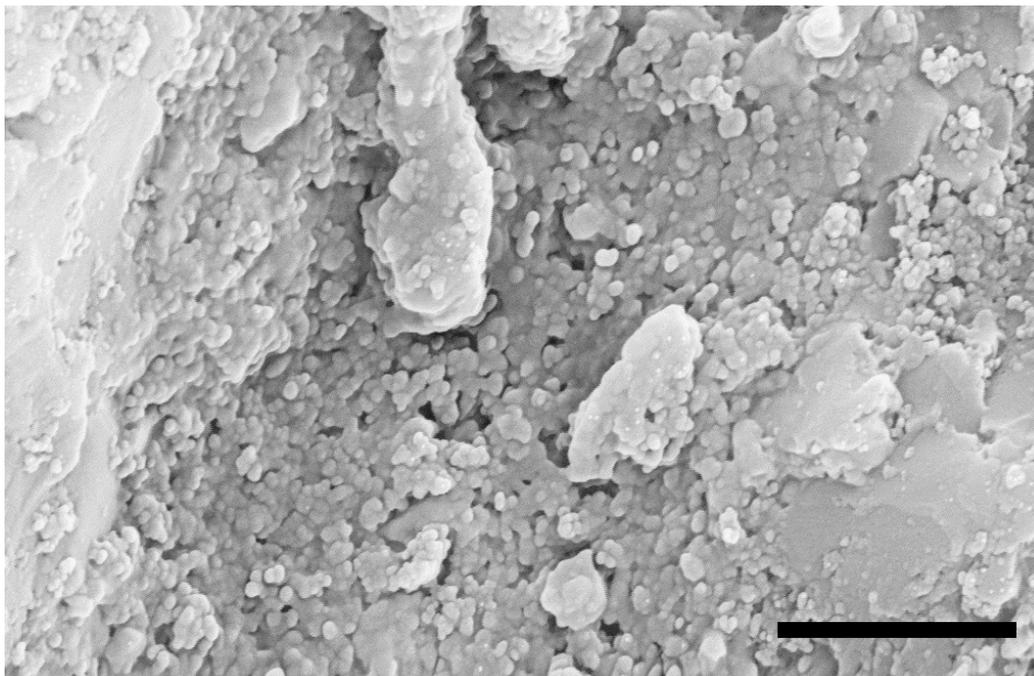


Figure 2. Scanning electron microscope (secondary electron) image of freshly broken surface of grayish-blue-colored Ellensburg blue. The surface is littered with sub-spherical to spherical particles inferred to be amorphous silica. The scale bar is 2 μm -long. Operating conditions: gold-coated, 30,000 \times magnification, 20 kV.

Conclusions. The blue-colored agate of Kittitas County, central Washington, comprises massive and banded specimens of chalcedony with minor moganite and amorphous silica. *In situ* agates occur in hydrothermally-altered basalt and are typically intergrown with calcite. Blue-coloration is inferred to result from Rayleigh scattering off 10s-of-nanometer-sized amorphous silica spheroids. The density of these particles is likely to be higher in specimens exhibiting a darker blue hue. While not unique, even in the United States as claimed by J.N.O. Thomson, the blue-colored agate of central Washington is particularly well colored and deservedly locally treasured.

Acknowledgements

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Chalcedonies and Jaspers used for Carving

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Gem carving has a unique standing in the world of art, as it is part of three art forms, the wearable *Jewelry Art*, the functional *Objects of Art*, which includes boxes, perfume bottles, frames, canes, etc., and the non-functional *Gem Sculpture*.

With about 100 different varieties between the two main quartz subspecies, the crystalline and the cryptocrystalline [crystals too small to be seen under the microscope], the quartz family is one of the most popular gem materials utilized by carvers world wide. Its hardness, wide range of textures and color varieties, crystal sizes, durability, availability, and often the affordability, make the quartz family gemstones irresistible and most attractive to carvers.

The cryptocrystalline varieties of quartz include the:

- Chalcedony group
- Agate group
- Jasper group
- Flint & Chert group
- Chalcedonic replacements, such as Tigereye or Petrified Wood

Although the agate family and the chalcedonic replacements belong under the “**Chalcedonies**” title, for the scope and length of this paper we will limit the discussion mainly to the monochromatic chalcedonies and the colorful jaspers, with a closer look at the popular **Ocean Jasper®**. We will talk about some of the chalcedony varieties, including **chrysoprase**, **blue chalcedony** in nodules or drusy, **gem silica**, **purple chalcedony**, **carnelian**, and **black chalcedony**.

The cryptocrystalline varieties commonly occur in veins, nodules, boulders, and drusy or botryoidal formations. [*Drusy* is a generic term for very small crystal mineralization, and *botryoidal* is grape like, bubbly]. The hardness, 6.5-7.0 on the Mohs scale, is high enough to allow for intricate carvings, high luster and good wearability. The chalcedony group comes in almost every shade of the rainbow. In general they show fewer patterns than their “cousins” the agates and jaspers. They may show hue and tone variations within the primary color, but they are best known for their uniformity.

Some chalcedonies are better known by their variety names, such as chrysoprase or carnelian, some with their color prefix, such as pink chalcedony, while others are known with their locality or mine name, such as Holley blue chalcedony. The gems with the most allure are the ones with the brighter and more intense colors and are consequently the most expensive. However, the pale colors referred to as “pastels”, depending on fashion and design, have their own attractiveness. The monochromatic chalcedonies are in general more expensive than agates, jaspers or flints, although some of those materials with rare patterns are highly desirable to collectors.

Jaspers are opaque fine to coarse grained cryptocrystalline quartz. They may be very granular and contain various inclusions, and are usually semi opaque to totally opaque, though often containing clear chalcedony areas. They are hard, tough and compact, with a uniform structure, and take a high polish, which makes them excellent material for lapidary work.

Jasper occurs as monochromatic material in many shades of red, brown, green, white and black and the variety names use the color prefix, i.e. Red Jasper. Many valuable jaspers are bright and colorful and have their own attractiveness to carvers. They may show unusual patterns and defined images in the stone, revealed when slabbed or cut open. The bands are not concentric, as seen in agates, but rather wavy, wider, uneven in width, spotty and wispy, and may contain wonderful swirls, lines, arcs or dendritic patterns which resemble “trees” or “forests”. The colors are often like a painter’s palette, which gives rise to imaginative scenes, figures, faces and animals.

When they exhibit a mixture of colors giving the impression of a landscape, they are then called **Scenic or Picture Jaspers**. They include the Owyhee jasper and the Biggs jasper. They are often “butterflied (slabbed consecutively and opened as mirror images), to make the “scene” larger.

When they exhibit spherical nodules (orbicules or orbs), dots or “bull’s eyes” (concentric rings of various colors and white) they are known as **Orbicular Jaspers**. They include the ‘**Leopard Skin Jasper**’, the ‘**Rainforest Jasper**’, the well-known ‘**Poppy Jasper**’, and the recently discovered **Ocean Jasper®** from Madagascar. Even though **Ocean Jasper®** has only been on the market for a few years, it has already become very popular with lapidaries. The many body color combinations, along with the beautiful natural vugs of white or green drusy quartz crystals and the stunning ‘orbs’ are features that can be skillfully used to create unique works. What makes this material so fascinating is that each piece of rough is completely different than the next, even consecutive slabs from the same chunk reveal different patterns.

Although the widespread use for **Ocean Jasper®** is the cutting of cabochons, eggs & spheres, medallions (round flats), large slabs with polished faces, display pieces, and beads, it is a wonderful material for carving. The incredible diversity of colors and patterns in **Ocean Jasper®** can be very inspirational to the creative spirit.

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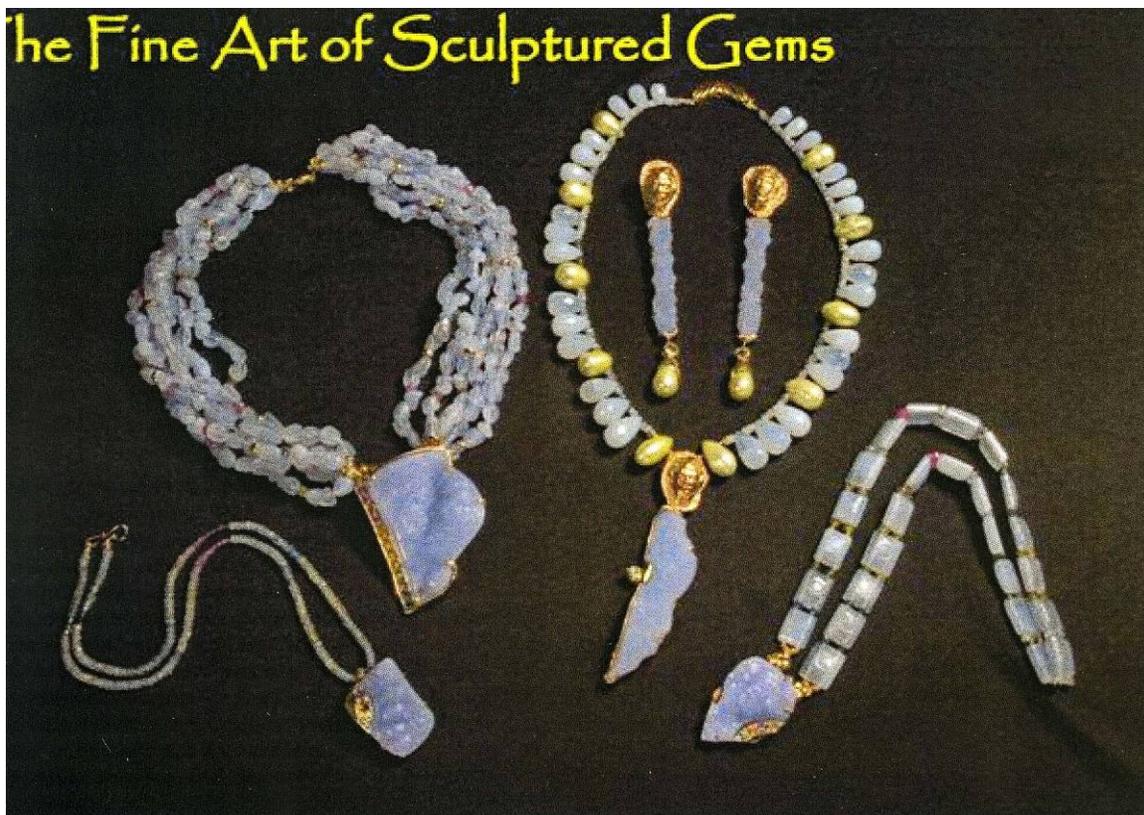
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The Fine Art of Sculptured Gems





Thinking about Thundereggs: An Historical Sketch of Inquiry into their Nature and Origin

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Putting aside the views of the Native Americans of Oregon's eastern Cascade Mountains, inquiry into the nature and origin of thundereggs as so named appears to have begun in the early 1930's as the classic Oregon specimens started to become widely known to the rockhounding community, but the first cut specimens, collected at Opal Butte in Heppner, Oregon in 1889, went on display in Spokane, Washington probably at least as early as 1908 and were shown at the Chicago World's Fair in 1893. For nearly 50 years after that, thundereggs were given little or no further attention. With the advent of rockhounding magazines such as *The Mineralogist* (1933) and *Lapidary Journal* (1947), honest, if sometimes bizarre, accounts of their origin were put forward by some of the geologically unsophisticated, with others contributing basically sound interpretations, and in time there came to be a modicum of occasional interest taken by geologists. For the most part, however, American geologists up to the present have with few exceptions taken little interest in thundereggs, there being so much else in late 20th century geology with which to be involved, but possibly also not wanting to be mistaken for a rockhound or because agate has had in America little standing as a mineral. Consequently, there remain errors of interpretation in otherwise excellent geological publications, such as when Maley (1994) portrays the thundereggs at Spencer, Idaho as "air cavities in rhyolite partially filled with precious opal."

By other names, however, speculation about the nature and origin of lithophysae (the term introduced by von Richthofen, who also introduced the term "rhyolite," in 1860) and of spherulites (Vogelsang, 1872), some of which today qualify as thundereggs, has been episodically engaged in since at least the mid-19th century. Several trends of inquiry stand out. The first collections appear to have been assembled in the first part of the 18th century from specimens collected in the German states of Saxony and Thuringia. Early scientific inquiry was carried on principally in England, France, and Germany, with occasional participation by American geologists. Major contributions were made by Delesse (1852) and von Richthofen (1860). Americans, however, with the main exceptions of Iddings and Cross, advanced their interpretations in relative isolation, so that Charles Palache in 1893 could describe "curious spherical masses" from a rhyolite in Berkeley, California, which then Dake in 1937, after the Oregon specimens came to attention, would describe as among the then recent and "earliest" noted occurrences of thundereggs, and Wahlstrom in 1941 could view the thundereggs of Specimen Mountain in Rocky Mountain National Park as "concretions." Between about 1850 and 1910 many of the early petrographers and petrologists (Zirkel, von Hauer, Cross, Bonney, et al.) took an interest in spherulites and lithophysae, as well as in the "globular felsites," "pyromerides," and quartz-porphyrines in which the structures conspicuously occurred. A particularly sustained discussion was carried on in the meetings of the Geological Society of London, featuring contributions by many geologists including the first woman petrologist,

Catherine Raisin, who in 1889 described what is clearly a thunderegg from Wales. In the first part of the 20th century Australians, principally Bryan and Kay, entered the discussion. Interest among American geologists during most of the 20th century was rare, but N. L. Bowen in the late 1920's engaged in an exchange of papers (mostly concerned with the issue of silicate fluid immiscibility) and Ross' 1941 paper is noted.

Two avenues of inquiry were followed in almost total isolation from the international conversation. The discovery of "biconoids" (now known to be the weathered out cores of thundereggs) in the Paso Robles, California area occasioned one of these lines of inquiry, in which the specimens were variously interpreted as concretions or pseudomorphs of certain minerals or organisms. The other, carried on in the pages of *National Geographic*, began with the discovery of giant spheres (which would now be termed "megaspherulites"), which some at the time viewed as man made, in the Mexican state of Jalisco.

Not to be omitted is Shaub's 1989 effort, following upon his 1979 articles in *Lapidary Journal*. Closer to the present time are the works of a number of Germans, who are heirs to perhaps the most sustained record of interest; the German best represented in recent years is Gerhard Holzhey. In 2002 Daniel Kile published a very good account of thundereggs in general and in particular the thundereggs from the Del Norte area in Colorado. Finally there is the Geode Kid's ongoing *magnum opus*, *The Formation of Thundereggs*.

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Ancient Agate Lore and Early Efforts to Explain Agate Formation

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Many theories have been advanced concerning the origins of agates; there is also a great deal of popular and medical folklore in this realm, which ethnom mineralogists have begun to explore. There have been a number of curious and amusing early theories of agates and agate formation, and an interesting question has been, trying to determine the actual location Theophrastus had in mind when he talked about the "Achatas River." in Sicily. There continue to be disputes about agate formation--a fascinating example of the sociology of scientific controversy. The author will discuss examples and conclusions from his work in progress, a history of agates and of popular rockhounding.

**A Review of "An Elementary Treatise on Quartz and Opal"
by George William Traill, 1870**

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Denzil Wiggins unearthed this rare 75-page hardbound volume from his collection at his shop in Lakewood, Red and Green Minerals. The frontispiece library plates show that this book originally belonged to Jesse Randall, famous Colorado mineral collector and newspaper man. An enthusiastic collector and mineral dealer, Randall played a vital role in the development of Colorado mineralogy for over 60 years, winning many medals for his displays, including a gold medal at the Columbian Exposition in Chicago in 1893.

Scottish collector George Traill produced his first compilation of quartz descriptions in 1866, then four years later produced this volume, dedicated to famous Scottish mineralogist M. Foster Heddle. Traill listed every species of quartz in proper taxonomic form with synonymies, descriptions, world-wide locations, museum collections, and localized names. He related ancient metaphysical lore and legends. Summarizing all information he could glean from historic references, Traill described standard treatment methods for the betterment of quartz, agates, and opals. He hypothesized possible origins of various forms of quartz and opal.

The earliest collection and exhibition of Colorado quartz, agate, and opal occurred simultaneously with the publication of this Treatise, although no Colorado locations are listed. In 1866, famed New York Herald Tribune traveler writer, Bayard Taylor, collected opal in Idaho Springs and moss agates in Middle Park. Prized jewelry made of Colorado agates was given as awards at early territorial fairs and horse shows. In 1867, Joel Parker Whitney won a coveted gold medal at the Paris Exposition with Colorado ore samples. He then donated the specimens to schools and museums throughout Europe, so Europe was aware of Colorado's treasures. In 1869, the British-Colorado Mining Bureau headed by Robert Old had a substantial cabinet collection in London which included quartz specimens from Colorado Territory.

The Treatise tells that an amazingly high level of quartz mineralogical research and knowledge existed 135 years ago. The book fills a gap in knowledge between the ancients and the mid-19th century and traces man's fascination with the very simple substance, quartz.

Chalcedony and Unusual Habits of Crystalline Quartz from Carbonate Concretions in the Alberta Badlands

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The Upper Cretaceous sedimentary formations exposed in “badlands” terrain along the river valleys of south-eastern Alberta are world renowned for their dinosaur fossils. Much less well known are the diverse forms of crypto- and macro-crystalline quartz that also occur in these formations. The best mineralization occurs in clay-ironstone (septarian) nodules that are prolific in some horizons of the middle to lower Horseshoe Canyon Formation. These nodules, which are up to 30 cm or more in size, locally show variable proportions of shrinkage cracks that host the mineralization of interest.

In some areas, the cracks are mineralized with honey-colored calcite. This fully coats crack surfaces and most commonly completely fills the cracks to create the characteristic internal structure of septarian nodules. Crystals growing into free space are moderately uncommon. Nodules in other areas show predominant mineralization by quartz, typically chalcedony with or without crystallized quartz. Chalcedony may coat crack surfaces, but it is commonly poorly attached. Deposition of quartz is generally discontinuous along the cracks, resulting in limited free space allowing for a quality of crystallization can be surprisingly good. Quartz crystals most commonly form aggregates that appear to have a single point of attachment or are recovered as floaters.

Chalcedony occurs in a variety of forms. These include thin crusts (typically simple crack fillings), less commonly botryoidal to irregularly rounded masses, rarely rosettes, and very rarely thin seams of translucent coarse fibrous material that is slightly chatoyant. It also forms as typically bluish overgrowths on petrified wood, in one small area including strikingly developed concentric ridges.

Chalcedony is also the precursor for two other forms of silica mineralization. Small beads appear to form the nuclei for the widely distributed, radiating aggregates of quartz crystals to be described later. Cubic crystals that are locally common are chalcedony pseudomorphs after what is believed to be pseudocubic melanophlogite. They occur typically on a substrate of chalcedony as sharp, simple cubes, rarely singles, more commonly as complex, intergrown groups that are colorless to opalescent white, with transparency and luster resembling that of the associated chalcedony. Cubes reach over 1 cm in size, but most, including those found on chalcedony overgrowths on petrified wood or rather less conspicuously at the edges of some very thin crusts or plates of chalcedony, are much smaller (mm size). All chalcedony appears to fluoresce under UV light with moderate intensity, more strongly under long-wave, typically medium- to strong-yellow, less commonly white.

Quartz crystals are found in a fascinating range of morphologies, essentially all of which appears to have formed from a single generation. Crystals of “normal” habit are distinctly uncommon as the predominant quartz mineralization, except locally within nodules that have open cracks lined with calcite crystals. Otherwise, with the exception of rarer drusy quartz, most crystals can all be broadly classified as “prismatic”, although morphologies are typically very complex.

Most quartz occurs as aggregates of crystals that are typically highly distorted. The fascinating catalogue of habits includes flattened, radiating aggregates (very common), parallel-growth aggregates (common), regular and reverse scepters (common), and hollow or skeletal crystals (rare). Sizes reach to over 10 cm for crystal aggregates, to 4 cm for individual crystals. Hollow and skeletal crystals show face widths to 2 cm, and scepters to over 5 mm in length. Crystal sizes are, however, typically in the size range of a few mm, so that fullest appreciation commonly requires 10x magnification.

The divergent aggregates that typically form the largest specimens occur as flattened, radiating fans (very common) or complete rosettes (reasonably common). Although these aggregates are basically two-dimensional, commonly both aggregates and individual crystals may be curved to follow the shape of the narrow host cracks. In contrast, the doubly-terminated, sub-parallel to parallel-growth bundles, are much less common, generally smaller, with crystals typically less distorted, and curvature is rare. In addition to the sceptering / reverse-sceptering and hollow or skeletal forms, crystals from both types of aggregates may show “terracing” on both prism and termination faces. These terraces form in parallel sets, with sharp to rounded edges, at varying angles but most commonly oriented across the faces (i.e. approximately perpendicular to the *c* axis).

The crystallization environment for quartz in quartz-rich Alberta septarian nodules appears to be characterized by preferential nucleation on chalcedony rather than ironstone, followed by growth generally at high rates, but with significant fluctuations and / or interruptions. Distortions in crystal structure are ascribed to a lower internal crystal symmetry corresponding to the lamellar structure of “Bambauer” quartz, and to the physical constraints of the typically very narrow shrinkage cracks. High concentrations of impurities, consistent with development of Bambauer quartz, were likely important factors in the formation of both sceptered crystals and the pseudomorphic chalcedony cubes.

Many of the same uncommon crystal habits and morphologies have been recognized in quartz from other localities worldwide. The highly flattened, radiating aggregates from Alberta appear, however to be unique, as is the generally high proportion of such crystals almost to the exclusion of crystals of normal habit. For the other localities, the predominant deposit types are septarian nodules, amethyst and rose quartz deposits. All of these appear to share a common low-temperature hydrothermal environment, likely along with fluctuations in crystallization conditions and rates, and in most cases with quartz showing Bambauer-type lamellar internal structure.

These occurrences are described by Menzies (1997). A more comprehensive article by Menzies and Frazier has been submitted to *Rocks and Minerals* magazine, with publication expected in 2006.

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Unusual Quartz Crystal Growth Habits

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This paper will review several unusual crystal habits of quartz. The first we'll discuss is that of "Pagoda" quartz from Young's River, Astoria, Clatsop County, Oregon. This area is part of the Columbia Plateau basalt flows "Pagoda" quartz was formed by growth of calcite oriented on the original quartz crystals, then at a later time these calcite crystals became pseudomorphs of quartz after calcite. The girdling bands of quartz have no relationship to the original crystal.

The next unusual crystal habit is very closely related to the first. It is "cut quartz" from Dalnegorsk, Russia. Here the quartz and calcite formed at the same time, and later the calcite was dissolved away leaving only the quartz.

Another location where "cut quartz" was collected by the author in May of 2005 is near Story, Montgomery County, Arkansas. This is a pay-to-dig open pit claim of G.W. Johnson. The cut quartz crystals are found in clay between sandstone layers.

"Faden quartz" is another unusual crystal habit. Faden is German for thread, which appears to run through the crystal. The faden is formed by a tectonic fracture of a quartz crystal and the subsequent widening of the fracture to form the faden. During this time just enough quartz-forming solution entered the fracture to form the faden. It consists of tiny oriented crystals of quartz that appear white because of water and gas inclusions. Some noted locations for faden quartz are Waziristan, Pakistan; Saline County, Arkansas; Graubunden, Switzerland; and Quebec, Canada. Another location was brought to my attention in 2002 by Dwaine Edington. These crystals are micro in size, seldom over 2 to 3 mm in size. They formed in the confines of small quartz-lined geodes from Chihuahua, Mexico; much more work needs to be done on this occurrence of faden quartz.

Gwindel or twisted quartz crystals are one of the more unusual quartz habits. They are one of the most studied, without any definite conclusion as to how they are formed. There are as many theories as there have been authors on this subject. We know that something "kicked the normal growth pattern of the crystal out of whack". A normal growth pattern for quartz is a spiral around the c axis, with growth 3 to 5 times that of the outer faces. However, the spiral growth of a gwindel is around one of the a axes, cause unknown. Noted locations for gwindels are the Dodo mine, Tyumen Oblast, Russia, and the northern part of the Swiss Alps.

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Creede Sowbelly Agate: Banded Amethystine Quartz and Chalcedony

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INTRODUCTION

The Creede mining district, Mineral County, Colorado is one of the best-studied American mining districts, largely because of the efforts of a team of geologists from the United States Geological Survey. In 1959, the Survey selected the Creede district to serve as a natural laboratory for an intense study focusing on mineral paragenesis, fluid inclusions, light stable isotopes, ore chemistry, age dating, and the hydrology of ore deposition.

In addition, the Creede district has become well known among mineral collectors as the home of spectacular (rhythmically?) banded amethyst and chalcedony specimens popularly known as sowbelly agate. This agate was deposited from the post eruption epithermal system as gangue material in the precious metal vein system of the district.

Sowbelly agate may host inclusions of several silver bearing minerals (native silver, acanthite after argentite, and polybasite being the most important) as well as fluorite and barite. During the early mining days, this mineral assemblage was often an important ore in the stopes of the Big Cave at the Last Chance mine on the Amethyst Vein system, but not all sowbelly contained silver (Emmons and Larsen, 1923). Rock that did not show visible silver mineralization was thrown on the mine dumps. Since that time mineral collectors have searched the Last Chance mine dumps for specimens of sowbelly agate. This slide lecture program will focus on utilizing the USGS studies to better understand Creede sowbelly agate.

THE SAN JUAN VOLCANIC FIELD

Beginning at about 35 million years ago, and continuing on for some five million years, a multitude of strato-volcanoes erupted andesitic lavas over most of the southern Rocky Mountains. The present day San Juan Mountains are, by far, the largest erosional remnant of this volcanic field. About 30 million years ago, the nature of the volcanism changed to immense silicic pyroclastic flows ejected from a series of calderas. The majority of these eruptions were centered around three volcanic centers located near present day Silverton-Lake City, Summitville, and Creede. Approximately one-third of the San Juan field calderas are mineralized (Steven and Eaton, 1975; Steven and Lipman, 1976; Lipman, 2000).

At Creede, eight (two are concealed) overlapping calderas poured out incredible volumes of pyroclastic debris during a 1.4 million year interval beginning at 27.8 million years ago. The Creede ore deposits are related to two of these pyroclastic episodes. The veins of the district occupy faults that roughly follow the keystone graben cutting the resurgent dome of the collapsed Bachelor caldera. Some 2 million years after the collapse and resurgence of the Creede caldera, a hydrothermal cell mineralized the system of graben faults (Steven and Eaton, 1975; Steven and Lipman, 1976; Lipman, 2000). The actual duration of the period of mineralization was short-lived, less than 10,000 years (Campbell and Barton, in review).

ENVIRONMENT OF THE CREEDE VEINS DURING ORE DEPOSITION

Hayba, Bethke, Heald, and Foley (1985) presented a modified version of the parameters of the OH Vein originally worked out by Barton, Bethke and Roedder (1977). The table is summarized below:

Environmental Parameters for the OH vein during Ore Mineral Deposition

PARAMETER	RANGE OBSERVED	VALUES USED FOR MODEL	DATA SOURCE
temperature	190 – 285 degrees C	250 degrees C	fluid inclusions
pressure	40 – 50 bars	50 bars	evidence of boiling in fluid inclusions
depth	450 – 600 meters	500 meters	estimate from pressure
salinity	4 to 12 weight percent	6 weight percent	fluid inclusions
Na:K ratio	7.4 – 9.9	9	fluid inclusion analysis
pH		5.4 (nearly neutral at 250 degrees C)	calculated from mineral assemblage

It is important to note that temperatures generally decreased from north to south along the Amethyst vein and that the OH vein intersects the Amethyst vein north of the Big Cave stopes of the Last Chance mine (Emmons and Larsen, 1923; Robinson and Norman, 1984). Boiling is generally thought to have been limited to the northern portion of the OH vein during deposition of the ore minerals, but there is evidence for short-lived boiling episode(s) during deposition of the sowbelly agate (Hayba, Bethke, Heald, and Foley, 1985; Campbell and Barton, 1996). Barton (personal communication, 2005) emphasizes that boiling episodes have not been identified from fluid inclusions. In spite of the fact that these parameters are not an exact fit for the portion of the Amethyst vein that contains sowbelly agate, the parameters are quite valuable in that they put us in the ballpark for the depositional environment of sowbelly agate.

Salinity of 4 to 12 weight percent is considered high for most epithermal deposits, so researchers took special pains to study the possible sources of mineralizing fluids. The model that was derived from fluid inclusions, light stable isotopes, and a geologic reconstruction calls for at least two, and possibly three sources for the mineralizing fluids. Source number one is a circulating hydrothermal cell with waters derived from Lake Creede, a closed-basin saline lake that formed a moat around most of the resurgent dome in the Creede caldera. Source number two is a zone of heated, fresh meteoric water overlying the ore zone that episodically entered the vein system from the north. Additionally, it is possible that a quantity of magmatic water may have entered the circulating hydrothermal cell at depth during vein filling. Current modeling calls for mixing of these waters as a trigger for deposition of the ore and gangue minerals (Hayba, Bethke, Heald, and Foley, 1985; Barton, Rye, and Bethke, 2000).

SOWBELLY AGATE

Sowbelly agate was deposited in the Amethyst vein system during the first three stages of the paragenetic sequence of ore mineralization. It is important to realize that this vein system

was not a simple vertical crack in the earth, but a dipping, winding affair partially filled with chunks of broken-off wallrock lodged between the vein walls. These chunks were then incorporated into the next mineral growth, usually assuming what can only be described as a topsy-turvy position in the new rock. Barton (personal communication) and Robinson and Norman (1984) speculate that sowbelly deposition proceeded, or was early in, the main high-grade ore B-stage. Sowbelly was most common in, but not entirely limited to, the southern portion of the Amethyst vein near its intersection with the OH and P veins. The relevant portion of the most current Table of Paragenetic Sequence is shown below:

Table showing Partial Paragenesis of Minerals in the Veins at Creede

STAGE	CHARACTERISTICS	DISTRIBUTION
Pre-Ore Potassium Metasomatism	Sodium & calcium in ash flow tuffs replaced by potassium, eliminating volcanic glass of the immediate area of district as source of silica	Throughout district
Ore Stage A (earliest)	Quartz with minor sulfides, chlorite, hematite & adularia Abundant rhodochrosite with quartz	OH, P & Amethyst veins Bulldog & southern Amethyst veins
Ore stage B (220-250°C in OH vein, but 150-200°C in Southern Amethyst vein) (main ore stage) (main sowbelly stage)	Galena, sphalerite, tetrahedrite, chalcopyrite, pyrite, silver minerals, quartz and chalcedony , barite, chlorite, hematite, and fluorite	OH, P, Amethyst & Bulldog veins Barite concentrated at southern end of system Chalcedony widespread but minor except in upper portions near the junction of the Amethyst, OH & P veins
Ore stage C (about 270°C in OH vein)	Fluorite, quartz , siderite	Principally in the OH, P, & Bulldog veins
Ore stages D & E	Stages D & E follow sowbelly deposition	

(Adapted and modified from Barton, Rye, and Bethke, 2000) (Temperatures by E. Roedder, summarized by Hayba, 1985 and 1993; Robinson and Norman, 1983; Hemingway, 1986)

Sowbelly agate is composed of alternating bands of cryptocrystalline chalcedony and crystalline quartz. As much of the crystalline quartz is amethystine, the banded structure may resemble sowbelly (salt pork or bacon) for which it was named by early Creede miners and prospectors. Barton and Bethke (personal communications, 2005) report occasional bands of opal, as well as non-amethystine milky and clear quartz. Some chalcedony is length slow and thus could be called quartzine. Chalcedony bands are arranged in radial or spherulitic growth patterns. In polarized light, some chalcedony is composed of clusters of spherulites instead of simple bands of radiating fibers. Length slow chalcedony (quartzine) is found both as spherulites and bands of fibers mixed with “regular” chalcedony. Some chalcedony probably replaces opal (Barton, personal communication, 2005) and certainly thin sections suggest that quartz may replace chalcedony. In addition to the standard white, chalcedony in sowbelly may be gray, purplish gray, and distinctly amethystine.

Bands of crystalline (often amethystine) quartz alternate with chalcedony bands. Bands of amethyst crystals are arranged with their c axes oriented in parallel to near parallel growth. The direction of growth is along the c axis and generally perpendicular to the vein wall, but curved along the spherulitic surface of the underlying chalcedony growth. The older literature often refers to this type of vein growth as comb structure. In cross-polarized light, some larger amethyst crystals (5mm to 1cm, plus) show zones of ghost chalcedony fibers near the crystal margin. A fringed zone of chalcedony fibers seems to leap like fire from the surface of the amethyst crystals. Barton (personal communication, 2005) calls the growths, appropriately, flame quartz.

The entire sowbelly structure grew from the vein wall into the open space toward the center of the vein. Many specimens from the mine dumps consist of only half the vein, terminating in a drusy comb of amethyst crystals. Specimens from places where sowbelly fills the vein exhibit a banded growth on either side of a centered plane, that is essentially a mirror image of its opposite. These specimens may exhibit a series of open vugs lined with amethyst crystals in the center of the vein, while other specimens show complete vein filling. Barton (personal communication, 2005) points out that where the vein dips toward the horizontal, the bands show an asymmetry from slumping in hanging versus footwall sowbelly growth patterns. Footwall bands may contain small piles of sediments trapped in chalcedony. Some specimens show markedly more chalcedony than amethyst, while others exhibit a greater abundance of amethyst.

Band-width varies dramatically for both chalcedony and amethyst, ranging from a millimeter (or less) up to several centimeters in thickness. Most specimens show a zone of very thin bands near the vein wall. Also, some bands of chalcedony (and occasionally crystalline quartz) show, internally, several very regular bands of iron oxide stains that may indicate a zone of sediment deposition (or even a fluctuating water level) during a period of chalcedony non-deposition. These bands run from one edge of a thin section to the other, cutting right across chalcedony fibers and leaving the optical continuity of the fibers undisturbed.

There have been periods of dissolution or leaching of minerals included by the sowbelly at some point in time. Based upon an examination of many specimens, I think that one period of dissolution occurred about half-way through the complete sowbelly depositional episode, as there are specimens that show a zone of bands with mold cavities and other zones of sulfide and native silver inclusions. During dissolution, the included minerals were completely leached, leaving open molds, often lightly coated with a thin crust of iron oxides and silica. I have not observed any later filling of these cavities with any other minerals, even though it seems fairly

obvious that a considerable amount of chalcedony and amethyst were subsequently deposited. The mold cavities are thin irregularly shaped openings, and the only clue as to what minerals were leached is that the etched crystals were not equant and probably consisted of blades, tablets, acute rhombs, needles, and finely crystallized intergrowths of various species. Based upon morphology and Plumlee's (1989) detailed mineralogy, likely candidates for etching would appear to be barite, calcite, siderite, chalcocite, native silver, and polybasite. Plumlee (1989) identified a major episode of barite leaching in the early portion of his stage 3. While his work centered on the Bulldog vein, it is certainly possible that we see an equivalent dissolution in the southern Amethyst vein. (I should point out that there is obviously another, later period(s) of dissolution that may coincide with supergene events.) Bethke and Barton (personal communication) report equant molds of both sphalerite and fluorite in sowbelly.

Brecciation of sowbelly and the enclosure of banded breccia fragments enclosed in later deposited bands is not uncommon. In fact, sowbelly encloses all sorts of broken-off chunks of more sowbelly, wallrock, and even stray crystals. The brecciation, however, is not a vein-wide event and thus cannot be correlated within the vein.

IONIC SOLUTIONS VS. COLLOIDAL SOLS

It is assumed that circulating Lake Creede waters took vast amounts of amorphous silica into solution through the dissolution of volcanic glass from the pyroclastic rocks of the district (Fournier, 1985; Hayba, Bethke, Heald, and Foley, 1985). The model of Hayba and others (1985) calls for deep circulation of these waters at temperatures perhaps as high as 450 degrees C. While it seems most likely that silica was carried in ionic solution, the solution may have achieved silica supersaturation with a resulting formation of a colloidal silica sol. It is important to realize that there are three parts to the problem:

1. Getting silica into solution
2. Silica transport
3. Silica deposition

The evidence for and against sols is contradictory. In support of sols, Paul Barton (personal communication, 2005) has observed some soft sediment slumping in some chalcedony bands in samples from the Amethyst vein, but soft sediment deformation is by no means a universally observed feature of the chalcedony bands in sowbelly agate. I have observed what appear to be zones of shrinkage cracks in chalcedony-rich portions of the banding, but this is not seen in all samples

Fournier (1985) and other researchers (see Fournier, 1985) emphasize the importance of mixing of relatively saline hot water with overlying less saline, colder water as a cause of precipitation of quartz. They also point out that a cold-water component may still be rich in oxygen from prior contact with the atmosphere. The presence of oxygen rich, meteoric water could result in oxidizing conditions producing amethyst with available ferric iron (Fournier, 1985). Again, the question of whether ferric iron exists as a colloidal sol of ferric hydroxide or a "normal" ionic solution remains unanswered.

It should be pointed out that flocculation of a colloidal sol may be easily initiated by the introduction of an electrolyte (Krauskopf, 1967). Bethke and Barton (verbal communication, 2005) emphasize that the chalcedony bands appear to have formed rapidly, while amethyst bands seem to have grown as crystals over a relatively longer period of time.

In spite of evidence that most of the sowbelly deposition resulted from mixing of mineralizing fluids, there is also good evidence for boiling in the early stages of sowbelly deposition. Small (2 mm to several centimeters long) pseudo-stalactites of chalcedony are found within some bands located near the wall rock portion of the sowbelly. The term pseudo-stalactite is used because the structures lack a central drip tube. Campbell and Barton (1996) proposed that these growths result from a condensed vapor phase dripping from overhangs occurring along vein walls above a boiling mineralizing solution. In order for this to occur, the vein would be partially filled with a silica rich brine solution and partially filled with a vapor phase. Steam from boiling would *partially* fill the open vein, condense on the walls, re-dissolve silica from the vein walls, and deposit that silica as water dripped and evaporated from overhangs in the same way that icicles form. In order for some of the dripping silica rich condensate to evaporate, the relative humidity would have to be below 100 percent in the vapor filled chamber. A boiling brine, instead of pure water, allows this to happen. After a brief episode of “drip” growth, the vein re-filled completely with liquids and deposition continued, enclosing the pseudo-stalactites within sowbelly agate.

Barton (personal communication, 2005) emphasizes that there are many difficulties in getting enough silica into solution and then back out of solution as vein deposits. At present he is working with eleven different parts of a potential model to explain sowbelly. We all await his results.

Finally, some sowbelly banding sequences are very regular. It is quite tempting to compare this banding to varved sedimentary sequences. The fact that circulation of meteoric waters from two sources supply the circulating hydrothermal cell, makes cycles of summer/winter, wet season/dry season, or an as yet unconsidered cycle, a possible contributor to the banding. And, as the nature of the two water sources varies so greatly, it is tempting to try to fit them into the question of ionic solution vs. colloidal sol.

In conclusion it would seem that bands of amethyst in sowbelly agate have crystallized from ionic solutions. It may well be that chalcedony bands have flocculated from colloidal sols, but such a process of deposition has yet to be proved. In either case, both the phenomena of mixing of waters and boiling appear to serve well as a trigger for most of the mineral deposition at Creede.

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Editors' note: Peter Heaney was unable to be present at this symposium, but he did kindly send this excerpt from an earlier paper. The temperature of formation of agate, and whether it forms from a gel or a solution, remain controversial subjects; this paper presents some of the relevant issues regarding agate genesis.

A Proposed Mechanism for the Growth of Chalcedony

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Excerpt from Heaney (1993), Contributions to Mineralogy and Petrology 115: 66-74.

Origin of Chalcedony: Previous Work

Discussions regarding the deposition of chalcedony generally have focused on two interrelated questions: 1) At what temperature does natural chalcedony form? and 2) What is the chemistry of the precursor fluid?

Precipitation Temperature

Arguments for relatively high temperatures of crystallization for chalcedony generally proceed from the assumption that the solutions from which chalcedony precipitates are created during the fractionation of volatiles from deeper-seated magmas (Sunagawa and Ohta, 1976; Flörke et al., 1982; Burchardt, 1986). These solutions are assumed to flow in geyser-like pulses, and they are thought to deposit chalcedony as isopachous coatings within rock vesicles in response to a drop in pressure as the solutions enter the open cavities. It follows from this hypothesis that the repeated layering characteristic of wall-lining chalcedony arises from hydrothermal pulsing. Experimental syntheses of chalcedony have been cited as support for precipitation at elevated temperatures: White and Corwin (1961) produced chalcedony at 400 °C and 340 b; Oehler (1976) performed runs at 100-300 °C and 3 kb; and Kastner (1980) obtained chalcedony at 150-240 °C. In addition, Blankenburg and Berger (1981) suggest formation temperatures for agatoid chalcedony in excess of 375 °C on the basis of a crystallite size geothermometer.

On the other hand, it may be noted that experimental syntheses of chalcedony typically are performed at elevated temperatures in order to decrease the processing time. Therefore, the experiments do not preclude the possibility that chalcedony can form in cooler environments. An oxygen isotope study of Jurassic agates from the Karoo volcanics in Namibia (Harris, 1989) places the deposition temperature in the range of 26-169 °C. Harris (1989) favors a temperature of 120 °C, but Saunders (1990) argues that a more realistic value for Jurassic $\delta^{18}\text{O}$ actually places the proper temperature in the range of 39-85 °C. The reanalysis of this data and the absence of textural evidence for boiling bring the results of Harris (1989) into closer correspondence with the stable isotope investigation of Fallick et al. (1985), who argued for

precipitation of chalcedony in Scottish agates at 50 °C from fluids with at least a component of meteoric water. The common occurrence of chalcedony with low-temperature clays also would seem to support the possibility of chalcedony precipitation at or below 100 °C. Harder (1993) observes that the green rind that surrounds many agates consists of celadonite, glauconite, and berthierine, and Ingerson (1953) describes chalcedony amygdules from Tertiary andesites in close association with nodules containing calcite, saponite, and montmorillonite. Similarly, chalcedony within Miocene silicified corals occurs with syngenetic palygorskite (Strom et al., 1981).

Thus, even though laboratory syntheses of chalcedony generally have been performed above 150 °C, much of the direct analytical data indicate that in at least some instances chalcedony forms naturally in low-temperature (<100 °C) environments from fluids that are partly or mostly meteoric.

Antecedent gel or solution?

The notion that chalcedony is preceded by a viscous silica gel was proposed at least as far back as Liesegang (1915), who successfully mimicked in artificial gels the colorful banding characteristic of natural agates. In addition, features reminiscent of soft-body deformation have led some scientists to posit a gelatinous origin for chalcedony. Specifically, bulbous dilatations adjacent to the cavity walls of agates (Einflusskanälen) and fortification structures have been attributed to distortion of a plastic medium (Shaub, 1955; Landmesser, 1988; Moxon, 1991). Moreover, the irregularly crenulated shapes assumed by some agates and translucent chalcedonies have been interpreted as evidence for a viscous precursor (Garlick and Jones, 1990). Chalcedony also has been synthesized successfully from precursor gels and opals (e.g., Oehler, 1976; Kastner, 1980), and a sophisticated model of dynamic crystallization for chalcedony concludes that the colloid that is antecedent to an agate nodule contains 1 g SiO₂ per cubic centimeter of gel (Wang and Merino, 1990). Assuming a silica density of 2.2 g/cm³, this silica "lump" would contain 64.7 wt. % SiO₂.

On the other hand, a number of observations argue against the possibility of a colloidal precursor. Electron microscopy experiments by Landmesser (1988) have demonstrated that actual Liesegang banding is extremely rare in agates. Indeed, it would seem significant that Liesegang could duplicate agate patterns in silica gels but not in silica solids; the integrity of the banding is lost during the desiccation process (FrondeL, personal communication). Likewise, the patterns observed in Einflusskanälen may be consistent with the role originally ascribed to them as influx canals for depositional fluids. These channels typically exhibit an entire agate sequence in miniature, and the bands proximal to the inflow tubes appear tapered in two-dimensional slices. Moreover, a number of researchers have demonstrated that the crenulated rinds of many "cauliflower geodes" actually are pseudomorphous after antecedent anhydrite (Chowns and Elkins, 1974; Milliken, 1979; Maliva, 1987).

The emplacement of viscous silica gels within their host rocks would also seem problematic. The suggestion of Blankenburg and Berger (1981) that chert xenoliths can survive the ordeal of burial, melting of surrounding rock, and extrusion without being dissolved or otherwise destroyed appears physically implausible. If the silica is not originally entrapped within the host rock, then it must be transported into the host. However, the typically narrow flow channels within host rocks apparently would impede the flow of thick gels into open gas

cavities. In addition, vugs that already have been filled with silica must present a physical barrier to subsequent invasion by viscous fluids, but agates that exhibit repeating sequences of chalcedony and drusy quartz are not uncommon.

In addition, siliceous gels typically do not transform directly to chalcedony. Numerous studies of the diagenesis of abyssal marine oozes (see Williams et al., 1985) indicate a crystallization sequence involving intermediate opal-A and opal-CT. These silica phases are not observed in radially fibrous chalcedony, even on a microscopic scale (Novák, 1947; Midgely, 1951; Frondel, 1962; Heaney et al., 1994). Opaline phases can be observed in horizontally banded onyx (Graetsch et al., 1985), but this material is equigranular microquartz, not radially fibrous quartz. Moreover, a preponderance of experimental data indicates that the diagenesis of opal-CT to chalcedony is not solid-solid; instead, it appears to involve dissolution of cristobalite and reprecipitation of chalcedony (Mizutani, 1966; Stein and Kirkpatrick, 1976; Williams and Crerar, 1985; Cady and Wenk, 1989).

It may be possible that silica-rich fluids flow from deeper within the earth into near-surface cavities and become highly viscous upon the sudden reduction in pressure and temperature (Flörke et al., 1982). Such behavior is typical of geyser fluids, which contain dissolved silica in the hundreds of ppm (Fournier, 1985). However, geyser fluids precipitate a siliceous sinter that is either amorphous or cristobalitic; as with marine silica gels, chalcedony is not deposited directly from these fluids.

These considerations tend to support the alternative possibility that chalcedony precipitates directly from a non-viscous mother fluid and not from a gel. The silicified corals and shells of the Hillsborough Bay Formation in Tampa, Florida, appear to provide direct evidence for this interpretation. A number of surveys of this fossiliferous formation (see Strom et al., 1981) indicate that silicification occurred in the shallow subsurface, probably from meteoric fluids. The chalcedony that has replaced the coral skeletons is structurally indistinguishable from agatoid chalcedony. Close observation of these partially silicified corals reveals sharp contacts between the original calcite and the replacement chalcedony, suggesting that dissolution of calcite was followed directly by precipitation of chalcedony. The existence of an intermediate fossilization stage involving a siliceous gel is not indicated.

Similarly, Lund (1960) dismissed the idea of a colloidal precursor for Hillsborough chalcedony based upon his examination of a silicified coral comprised of two separated chambers. One of these chambers contained only drusy macrocrystalline quartz, and the other was filled with wall-lining chalcedony. These two quartz varieties clearly precipitated under nearly identical conditions of pressure and temperature. The only distinction that Lund (1960) observed between the two chambers was the presence of a hole in the cavity containing chalcedony. Lund (1960) concluded that the hole served as a conduit for the continual infilling and egress of solutions of dissolved silica, resulting in the precipitation of chalcedony. The sealed chamber received only what could diffuse through its cavity walls, and drusy quartz was formed instead.

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