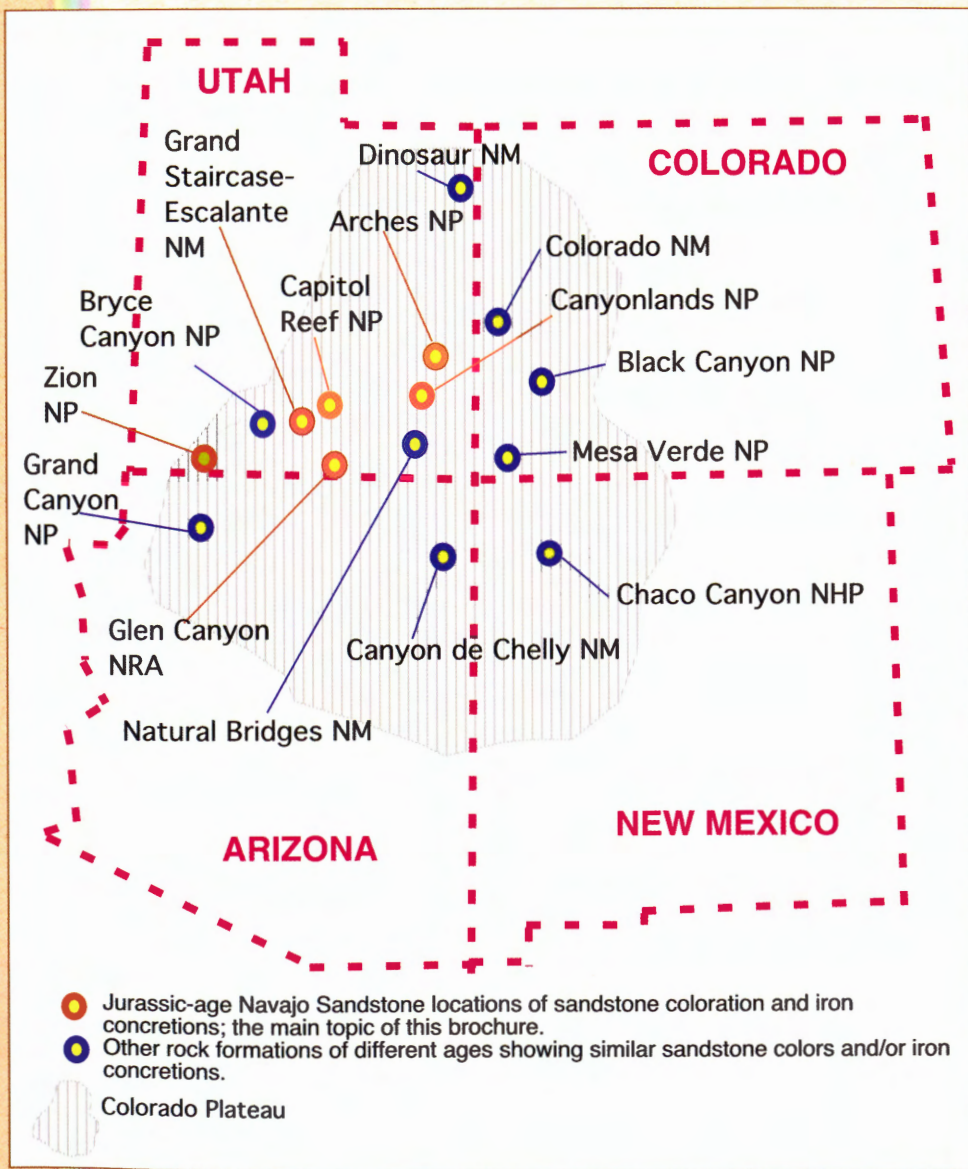


Rainbow of Rocks



*Mysteries of Sandstone Colors and Concretions
in Colorado Plateau Canyon Country*

By Marjorie A. Chan and William T. Parry



Colorado Plateau region centered around the Four Corners where the states of Utah, Colorado, Arizona, and New Mexico meet. Red rock canyon country is particularly well exposed in southeastern Utah. Localities are not inclusive, but are examples where sandstone coloration and concretions are found. NP= National Park; NM = National Monument; NHP=National Historical Park; and NRA=National Recreation Area.

Cover photo: Glen Canyon National Recreation Area and Lake Powell, with colored Jurassic-age sandstones by the Utah-Arizona border. Photo courtesy of Doug Sprinkel.

Brochure design by Vicky Clarke.

Introduction

Sunrise illuminates Colorado Plateau's canyon country. In the early morning light, cliffs radiate a rich red glow, and a sculptured panorama of sandstone is revealed in a rich palette of crimson, vermilion, orange, salmon, peach, pink, gold, yellow, and white. Nearby are black, spherical rock marbles (iron concretions) collecting in small depressions, like puddles of ball bearings. These natural spherical balls have been called various names such as iron nodules, iron sandstone balls, or moki marbles. However, we use the name "iron concretion" to describe both the composition (iron oxide that is the dark mineral which cements the sandstone grains) and the formed shape (concretion).

What paints the sandstone such rich colors? Why is red a dominant color? Where do the black marbles come from? How did the black marbles form? Is there a relationship between sandstone colors and the marbles? This booklet explores the answers to these questions and poses other questions yet unanswered.

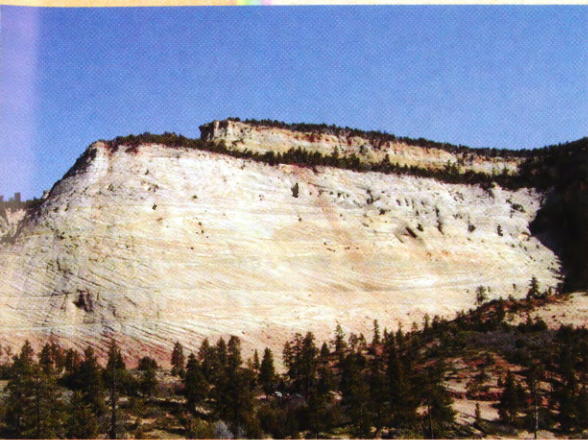
The Jurassic-age Navajo Sandstone exhibits a wide range of colors from shades of red to stark white.



In a privately owned area near Moab (southeastern Utah), the Navajo Sandstone is a pale orange, unbleached color. Only 10 miles (15 km) to the northwest of this picture, the upper portion of the Navajo Sandstone formation is bleached white.



The Boulder-Escalante area (south-central Utah) exhibits broad expanses of white Navajo Sandstone.

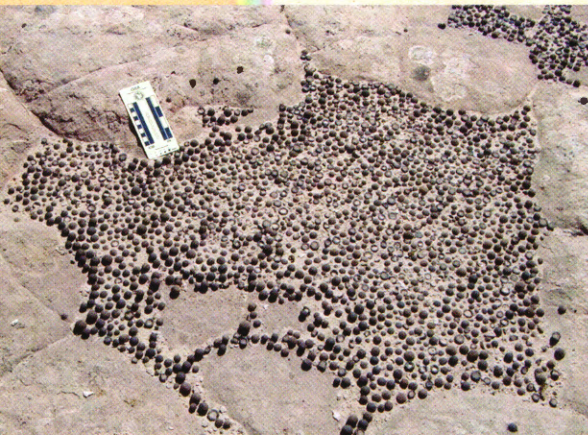


In Zion National Park (southwestern Utah), the upper Navajo Sandstone is mostly white with shades of yellow.



Both pale orange and bleached white sandstone coloration in Grand Staircase - Escalante National Monument, Utah.

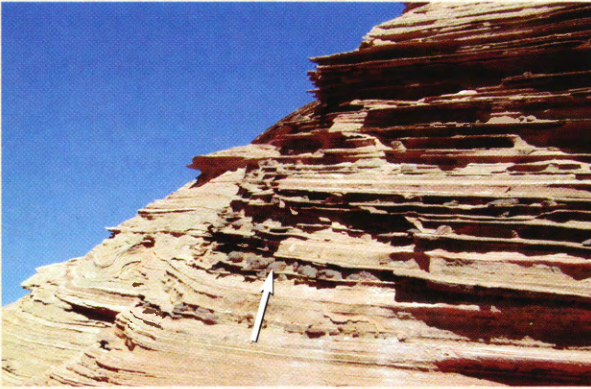
Iron concretions in the Navajo Sandstone.



Discrete, small, pea-sized "marbles" accumulated on a flat sandstone surface. Scale card = 6.5 inches (16.5 cm) long. Location: Grand Staircase-Escalante National Monument, Utah.



Partially developed iron concretions that resemble spotted measles dotting a sandstone outcrop. Scale card = 6.5 inches (16.5 cm) long. Location: Antelope Island, Lake Powell, Glen Canyon National Recreation Area, Utah.



*Grapefruit-sized, in-place, iron concretion balls (arrow).
Location: Antelope Island, Lake Powell, Glen Canyon
National Recreation Area, Utah.*



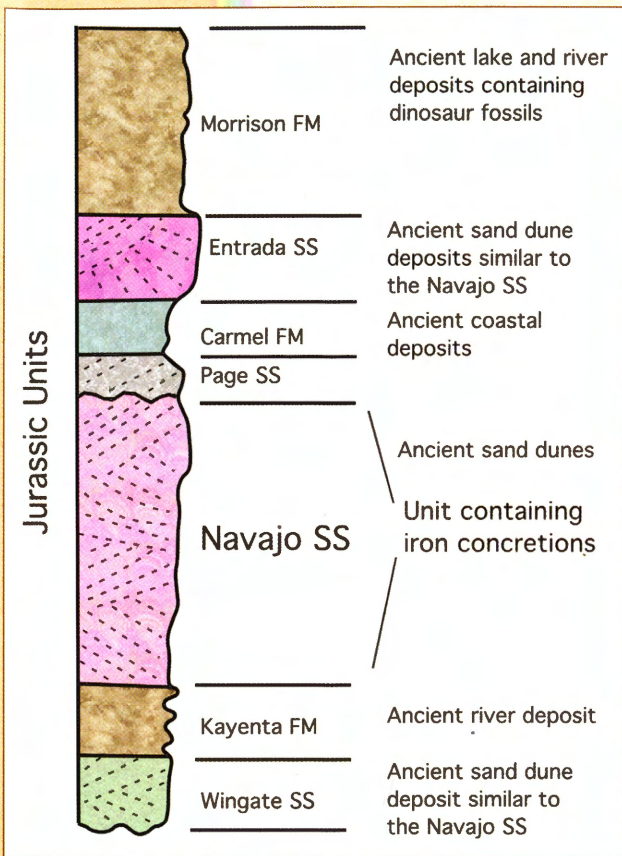
*Columns of iron-cemented sandstone.
Location: 10 miles (15 km) northwest of Moab, Utah.*

*Crinkly sheet of iron-cemented sandstone within the ancient
sand dune bedding (outcrop is 10 feet or 3 m high).
Location: Grand Staircase-Escalante National Monument, Utah.*



Red Rock Country

Sandstone can exhibit many colors, but landscapes of the American Southwest that exhibit such striking shades of red have been informally called "red rock country" (portions of which are also called "canyon country" where deeply incised canyons exist). The rock unit called the Navajo Sandstone features prominently in this landscape, and contains some of the largest and most abundant iron concretions found anywhere in the world. The Navajo Sandstone was named for the "Navajo country" of Arizona, Utah, and New Mexico. The red rock country on the Colorado Plateau where the Navajo Sandstone and other relat-



Some Jurassic rock formations in the Four Corners region of southeastern Utah, with emphasis on the Navajo Sandstone. The ancient environments represented in the rock units are given at the right. Modified after Hintze (1988). SS=Sandstone, FM=Formation

ed rock formations are prominently exposed is centered around the Four Corners region where the states of Utah, New Mexico, Colorado, and Arizona meet. This story of the red rocks started millions of years ago. In the next section "Long Ago and Far Away," we address the following six questions.

1. Blood of the Living Rocks: What colors the sandstone red?
2. The Crimson Source: What is the origin of the red pigment?
3. Big-Time Bleaching: What happened to make some red sandstone turn white?
4. The Iron Baby: Where did the red pigment go, and what do iron concretions have to do with this?
5. The Light of Day: How were the sandstones exposed at the surface in the present landscape?
6. The Time Machine: When did all of this happen?

Long Ago and Far Away

This story begins millions of years ago in a world and landscape very different from today: during the Jurassic Period (144-206 million years ago) when the North American continent was at a different latitude, and Utah was close to the equator in a belt of strong trade winds. These winds moved quartz sand to build dunes that covered an area bigger than the Sahara Desert. An accumulation of desert sand dunes is called an erg or sand

sea. The largest erg to ever exist in North America is preserved in the Jurassic-age Navajo Sandstone (approximately 180-190 million years old) that is up to 2,500 feet (750+ m) thick. The Navajo Sandstone was deposited over a broad area of the Colorado Plateau and is now well exposed in national parks and monuments such as Zion, Capitol Reef, Arches, Canyonlands, Grand Staircase-Escalante, and a number of surrounding areas. Other rock formations such as the Wingate Sandstone and Entrada Sandstone (see figure of Jurassic units) are also ancient sand dune deposits that show similar coloration and iron concretions. However, the Navajo Sandstone is the focus of this booklet because it displays such a wide range of color (from white to many shades of red) and contains some of the greatest variety of iron concretions found anywhere in the world.

1. Blood of the Living Rocks

What colors the sandstone red? The red color is caused by a union of iron and oxygen (an iron oxide) known as hematite (Fe_2O_3), a mineral named from the Greek word for blood. Iron is a powerful pigment present in many sediments and rocks, thus it commonly imparts color to the rocks. Although red is the common pigment color, not all iron oxides are red; some are brown or yellow (minerals - limonite or goethite), and some are black (mineral - magnetite). Some iron minerals are metallic yellow (mineral - pyrite consisting of iron sulfide) or green (minerals - chlorite or clay consisting of iron silicate).

Although geologists have long understood that sandstone coloration is a function of varying amounts of iron, it is only recently that scientific studies (partly presented here) detail how this happens.

2. The Crimson Source

What is the origin of the red pigment in sandstone? The origin of the color is due to a chemical reaction similar to rusting of a nail. An iron nail appears silver in color and metallic. When a nail rusts due to the addition of water molecules and oxygen, two or three iron electrons are lost to oxygen (the iron is oxidized). The remaining electrons,

together with the oxygen, absorb all of light's colors except red and brown. But iron nails don't color sandstones red.

Sandstone originates from the breakdown of older rocks, a process called weathering. Granite, for example, is a type of igneous rock that commonly breaks down in weathering to produce sand grains that later make up sandstone. The older "parent" rocks often have minerals that contain some iron, but these minerals are green or dark brown. Water in con-



Modern desert sands in Western Australia showing an early red coloration from thin coats of oxidized iron around individual sand grains. Photo courtesy of Dick Ojakangas.

tact with the atmosphere absorbs oxygen. Dissolved oxygen in water is very aggressive in removing electrons from iron to produce rust (oxidized iron). As the iron-bearing minerals weather and react with oxygen and water from the atmosphere, the iron is released and forms very thin, paint-like coatings of hematite on the quartz sand grains. Iron in hematite that has lost three electrons absorbs most of the visible colors of light and only red is transmitted to produce the mineral's red coloration. Sands deposited in deserts gradually redden as iron minerals break down and lend their red coloration to the sand. The reddening continues after burial as

more overlying sedimentary units are added. Over millions of years, these loose sand grains are compressed and cemented into the rock called sandstone. In these red sandstones, microscopic, oxidized iron films of the mineral hematite spread and coat the quartz grains. The amount of hematite is very small, but since iron is a powerful pigment a little red goes a long way!

3. Big-Time Bleaching

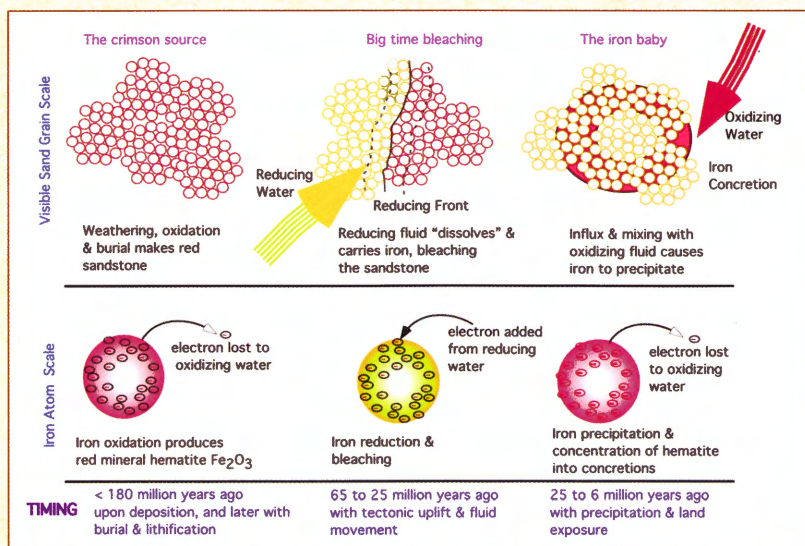
What happened to make normally red sandstone white? Sandstone is porous and permeable because there are holes or spaces between sand grains. Sand dunes make particularly permeable sandstone because wind effectively sorts the grains to create a homogeneous deposit with uniform grain size and not much fine-grained pore fillings. Given

enough pressure and force, water moves relatively easily through porous sandstone almost like water through a sponge. Even during heavy rains with much surface runoff, some water infiltrates the sandstone. Under certain conditions, iron pigment will dissolve in water and be removed, or be rendered colorless by chemical reactions with the water. This is much like a bleaching detergent permeating a red cloth, removing color as it spreads. (However, household chlorine bleach won't take out iron rust stains because chlorine is not chemically able to move iron).

How does bleaching happen chemically? Some waters contain reducing agents (electrons are added to the iron atom and oxygen is removed) that make the iron soluble (dissolvable) in water. To make iron soluble, the water can restore one of the electrons that was lost by iron during early weathering and oxidation. Fluids such as hydrocarbons (petroleum), weak acids (vinegar-like), or those with hydrogen sulfide (gas that smells like rotten eggs) can also restore an electron to iron, thus these are called reducing waters. This water can dissolve and remove nearly all of the hematite and bleach red sandstone to white.

Sandstone Coloration is:

- A function of varying amounts of iron (mineral hematite - Fe_2O_3) that imparts red color.
- Initially red, soon after sand grains are deposited and buried.
- Red where thin scattered films of hematite coat sand grains, and white where the thin films of hematite have been removed by bleaching.
- Facilitated by how easily fluids can move through a sandstone due to different textures of the sandstone (e.g., how loosely or tightly sand grains are packed together).
- Variable even on a scale of fractional inches where thin red layers alternate with white layers. This is again a function of microscopic textures in the sandstone.
- Affected by oxidizing fluids that encourage hematite precipitation (red color) as well as reducing fluids that bleached the sandstone by removing the hematite (white color).
- A property that may have changed over time and involves fluids and processes that occur over tens of millions of years.



Summary of the timing of events related to the sandstone coloration and iron concretions.

Sharply contrasting sandstone coloration within the Navajo Sandstone.



Navajo Sandstone within Snow Canyon State Park exhibits red sandstone with only small bleached white areas (upper center). Photo by Bruce Simonson.



North of St. George near Snow Canyon State Park (southwestern Utah), the upper Navajo Sandstone is white with some irregular pockets of red sandstone that likely represent the original sandstone color before bleaching.



Navajo Sandstone within Snow Canyon State Park exhibits bleached sandstone with a swath of red sandstone that likely represents the original color before bleaching. Photo by Bruce Simonson.

4. The Iron Baby

After bleaching, (A) where did the red pigment go, and (B) what do sandstone marbles have to do with this?

(A) The red pigment is essentially “dissolved” but still carried by reducing water. So the iron that was bleached out of the sandstone is “held” by the reducing water. On a chemical level, critical changes may occur in the water that has dissolved the iron pigment.

(B) Once the reducing water carrying the dissolved iron meets and mixes with oxygenated water, the oxygen immediately removes an electron from the dissolved iron and drastically reduces its solubility. Thus, a new iron mineral, hematite containing fully oxidized

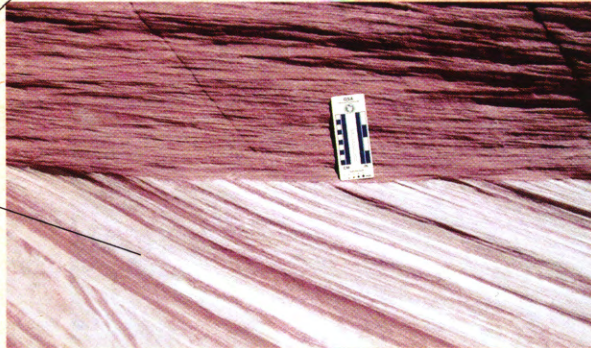
Navajo Sandstone coloration where the fluid movement and hence the colors are controlled by inherent rock properties displayed in Grand Staircase-Escalante National Monument, Utah.



Bleached white and yellow coloration where reducing water bleached the lower white sandstone.



Red and white "striping" coloration from preferential movement of fluids through sandstones.



iron, is immediately precipitated in the spaces between the grains of the sandstone to form the iron concretions. This is like a marriage where opposites attract and the end product is a new "baby"; the mixing of water causes new iron minerals to grow or precipitate.

Now, instead of thin iron coatings on the sand grains, the iron is concentrated as a thick hematite cement, like a glue, that surrounds the quartz sand grains. Thus, the most abundant iron concretions are typically found in areas where the sandstone is bleached, most likely because the iron for the concretions is actually some of the same iron that formerly made the sandstone red.

Precipitated iron can cement sandstone into many different sizes and shapes of concretions. Pea- to marble- to baseball-sized iron concretions are some of the most striking

Marble to golf ball-sized iron concretions from the Navajo Sandstone, Grand Staircase-Escalante National Monument, Utah. Total length of scale bar = 2 inches (5 cm).



Nearly perfect spherical balls of hematite-cemented sandstone.



The inside of spherical balls. Pink sandstone makes up much of the interior, and the outer dark rind is cemented by iron oxide (hematite).



Other fantastic shapes of iron concretions.

forms, but buttons, columns, pipes, towers, and even corrugated sheets or layers are some of the other shapes that can form. The precipitated hematite can be so concentrated that it looks black in reflected light, but it is still red in transmitted light when viewed under a microscope.

We don't know why some iron concretions are so round, but perhaps some "seed" or nucleus alters local chemistry to precipitate iron in a uniform (spherical) manner. In the concretions, the nucleus could be organic matter or other material that enhances chemical reactions and precipitation. Precipitation is most easily accomplished when some nucleus is present. However, if no nucleus is present, then there may be some optimum physical spacing of concretions that grow by drawing and pulling in their chemical components for precipitation from a local vicinity. Thus, when reducing water carrying soluble iron meets with oxidizing water, the concentrated hematite may precipitate in spaced-out spherical concretions.

All of this iron dissolution and transportation takes place underground. Even mixing with oxygenated water is a subsurface process. The precipitation of the iron in concretions takes place hundreds of feet or more below ground.

The ancient dune sandstones, because of their porosity and permeability, are a good medium for transmitting fluids. Water transport can also be facilitated along weaknesses and cracks in the rock (like faults and joints).

Over the long history of these rocks, enormous amounts of water have flushed through this porous sandstone. The forma-

tion of one golf-ball-sized iron concretion requires many times its volume of water.

5. *The Light of Day*

How was the sandstone exposed in the present landscape? Originally, much of the sandstone was deposited as sand dunes in a desert 180 million years ago. Other rocks about the same age were deposited near the ocean when this region was near sea level. Why is the area now at considerable elevation above sea level and what processes or events led to its present elevation? Strong forces responsible for uplifting buried rocks are commonly attributed to the interactions between large outer pieces of the Earth's crust; a field of study called plate tectonics. Interaction of the Pacific plate (beneath the Pacific Ocean) and the North American plate (largely the continent of North America) thickened the crust and uplifted the Colorado Plateau 80 to 50 million years ago. Uplifted rocks were gradually removed by weathering and erosion, exposing the formerly buried rocks.

More uplift related to rising magma (molten rock) occurred on the Colorado Plateau about 25 million years ago (Ritter and Smith, 1996; Wendlandt and others, 1996). Igneous rocks resulting from the rising magma form prominent landmarks such as the La Sal Mountains, Abajo Mountains, and the Henry Mountains in Utah; the San Francisco Mountains in Arizona; and Shiprock in New Mexico.

During these episodes of uplift, and later during accelerated erosion beginning about 6 million years ago (Hunt, 1969; Lucchitta, 1979), the sandstone formations have been carved and sculpted by flowing water and river systems, including the Colorado River and its tributaries. Weathering and erosion have helped further expose sandstone cliffs over the past several million years.

Iron Concretions are:

- *Natural balls and other shapes formed in a porous sandstone.*
- *Made up of hematite (iron oxide) cement that precipitates around quartz sand grains.*
- *Likely comes from iron that was bleached out of red sandstone.*
- *Formed from the mixing of different fluids: reducing water carrying iron interacted with oxidizing water that induced the iron precipitation.*
- *More resistant to weathering (i.e., harder) than the quartz sandstone host rock.*
- *Unusual and can look "out of this world," but are formed by Earth processes over many tens of millions of years.*

Iron concretions are also known by other names (not inclusive) such as:

- *Hematite or iron nodules*
- *Iron sandstone balls*
- *Moki or moqui (term used by early Spanish) marbles*

Continued uplift and river cutting help to create the canyon country of the Colorado Plateau. The hard, spherical iron concretions are more resistant to weathering than the lightly cemented sand grains of the surrounding or encasing rock. Discrete, individual concretions, that are now loose like marbles, became concentrated on the surface because all the surrounding rock weathered away over a long period of time.

6. *The Time Machine*

How far back in time must we travel to see all of this happen? The sand dunes first piled up in the Jurassic deserts some 180 million years ago. The sands were red when they accumulated, and reddening continued for tens of millions of years during burial, compaction and cementation to form rock. The bleaching of sandstones probably occurred between 65 and 25 million years ago. The precipitation of iron concretions occurred after bleaching, likely between 25 and 6 million years ago.

We can apply basic principles of geology to deduce the relative time of bleaching. Regional rock colors follow the original layered patterns and have been later cut by rivers, to suggest that bleaching occurred before river erosion. However, some bleaching likely occurred after the formation of faults that provided easy pathways for fluid movement and localized bleaching along the faults and other fractures in the rocks.

A variety of scientific methods can be used to deduce the age of events in millions of years. Specific ages of rocks can be determined from the constant decay of radioactive elements in the rock minerals. A clay mineral called illite occurs along the faults that act as major conduits for fluid movement and bleaching of sandstones. The illite contains potassium, and thus its age can also be estimated. Potassium and argon age analysis of illite from the Moab fault (northwest of Moab, Utah) suggests that bleaching occurred as early as 50 million years ago when the fault developed, well before the time of the iron concretion precipitation.

Radiometric dating of minerals associated with iron concretions can help tell us when

the minerals were precipitated. Measurements of potassium and argon in associated manganese minerals (Chan and others, 2001) yield ages of 25 to 20 million years, and suggest a similar timing for some of the iron precipitation.

Paleomagnetic dating is a technique that relies on the memory that rocks have for the Earth's magnetic field. Iron minerals in rock act like a magnet and align themselves with the Earth's magnetic field, and the magnetic field has switched poles throughout geologic time. Measurement of the magnetism that remains in the rocks can indicate when they were deposited, and magnetism that remains in bleached rocks is an indication of the time of bleaching. Magnetic measurements (R. Garden, written communication, 2000) suggest the iron reduction and bleaching happened 65 million years ago or less.

Use of Iron Concretions

Iron concretions have a place in human history as well as geologic history. Findings of small spherical to irregular iron concretionary nodules are commonly cited in many archeological reports covering the prehistoric Four Corners area. At Canyon De Chelly National Monument in Arizona, iron concretions found at ancestral puebloan villages range in size from a few centimeters in diameter to large nodules with grinding facets on multiple surfaces. These are believed to be part of medicine bundles used for ceremonial purposes during both prehistoric and historic periods (Judd, 1954). Some concretions also may have been used as cooking stones (Barnett, 1973), hammerstones and ornaments (Mathien, 1997), or simply as unmodified nodules collected as "... curiosities and in part as objects of veneration (Cattanach, 1980)." Ancient people collected iron concretions and softer, stained mudstone and soil that was ground for the dye color that could be obtained from the iron.



Native American pictographs using the hematite pigment, likely from either iron concretions or iron-rich sediments. Location: Horseshoe Canyon, Canyonlands National Park, Utah.

Ground hematite was mixed with water to make paint and pigment for use on rock and plaster walls (Schaffsma, 1980). This pictograph artistry of the Native Americans is strikingly preserved on cliffs and within prehistoric buildings of the Four Corners region.

Over the Rainbow

What a mind-boggling idea: in some bright white sandstones of canyon country, all the scattered iron that originally made the sandstone red has been bleached and concentrated into compact iron concretions instead! Lots of reducing water had to push through the porous sandstone to bleach and remobilize hematite (some probably moved along fault conduits). Upon meeting up with oxidizing water, hematite was re-precipitated as some of

the fantastic iron balls, buttons, pipes, and columns that can be seen in sandstones of the southwestern national parks and surrounding landscapes. Large regional patterns of sandstone coloration reflect different types of fluids that have moved through the rocks in the past, and the chemical element iron is the telltale sign.

In addition to the large regional patterns of sandstone coloration, many rock formations contain localized coloration in sandstone that could be due to the presence of organic matter. Typically the host sandstone or mudstone is a red to yellow color, again from early oxidation and evenly scattered

iron. Ancient pieces of plant material or even large trees and roots in the host rock can be areas of locally reducing conditions because of the organic acids originally contained in the living matter. Thus, the organic material provides a locally reducing environment that may cause the host rock surrounding the organic material to be light green to white in color. In other instances, organic matter can locally enhance iron precipitation, as seen in iron-cemented burrows of Chaco Culture National Historical Park, New Mexico. Here, bur-



Bleached, reduced zone of light-colored sand around a cemented piece of organic root material, Navajo Sandstone in Navajo Canyon area of Lake Powell, Glen Canyon National Recreation Area. Scale card = 6.5 inches (16.5 cm) long.

rowing organisms (some similar to shrimp) may have dug into shoreline sands. The organic matter in the fecal pellets of the organisms may have provided the right local conditions of mixed reducing and oxidizing waters to precipitate the iron. Some of the concentrated iron in the burrows may actually be the iron that was originally disseminated and distributed in the shoreline sands.

Why does the Navajo Sandstone have the most abundant concretions compared to some of the other Jurassic sand dune deposits? The Navajo Sandstone is a special rock unit that has relatively consistent properties of porosity and permeability that make it one of the best reservoirs (rock that can hold fluids) and one of the best aquifers (rock through which fluids can flow) of the Colorado Plateau. The reason why the Navajo Sandstone contains such varied coloration and has abundant concretions is certainly related to the fact that it was a unit through which a variety of fluids could easily move.

The story is not over. Although we now have begun to

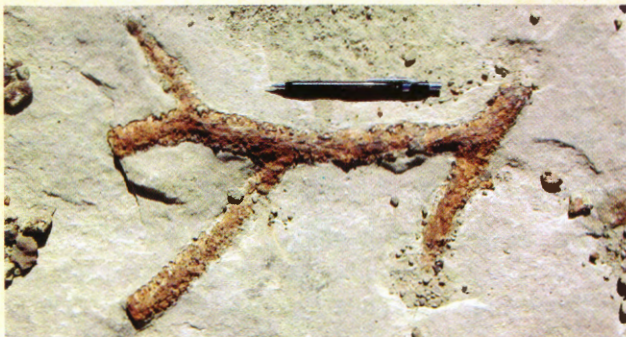
Other rock units on the Colorado Plateau show a variety of iron concretions. A unit younger than the Jurassic formations contains ancient shoreline sandstones exposed in the Cretaceous-age Mesa Verde Group, Chaco Culture National Historical Park, New Mexico.



Outcrop of iron-oxide concretions (dark areas) in light-colored sandstone.



Other odd concretionary features (not burrow related).



Ancient burrows made by a shrimp-like organism are later cemented by iron oxides, including hematite. Organic matter related to the burrow organisms provides a locally reducing environment that mobilizes the iron. Iron is precipitated at the interface upon contact with oxidizing water.



Remaining Mysteries Scientists are still working on:

- *Why are sandstone marbles so spherical?*
- *What determines the concretion size and shape? Why are some concretions nearly solid hematite cement, and other concretions have only a hematite-cemented rind with an "uncemented" sandstone interior?*
- *Is there any nucleus or seed that starts a marble growing, and if so, what is it? In some cases, iron may be preferentially attracted to areas that contain organic matter.*
- *What determines the clustering and spacing of concretions?*
- *What are the large-scale distributions and controls on both sandstone coloration and concretions?*

understand the sandstone coloration and the creation of iron concretions, there are still many remaining questions, such as the specifics of forming the round sandstone marble shapes. As new scientific techniques are developed, and future geologic studies of these sandstones are broadened, geologists will continue to probe into the mysteries at the end of the colorful sandstone rainbow.

NOTE: Special written permission and permits are required to collect or remove any rocks or concretions from protected areas such as parks and monuments.

Acknowledgments

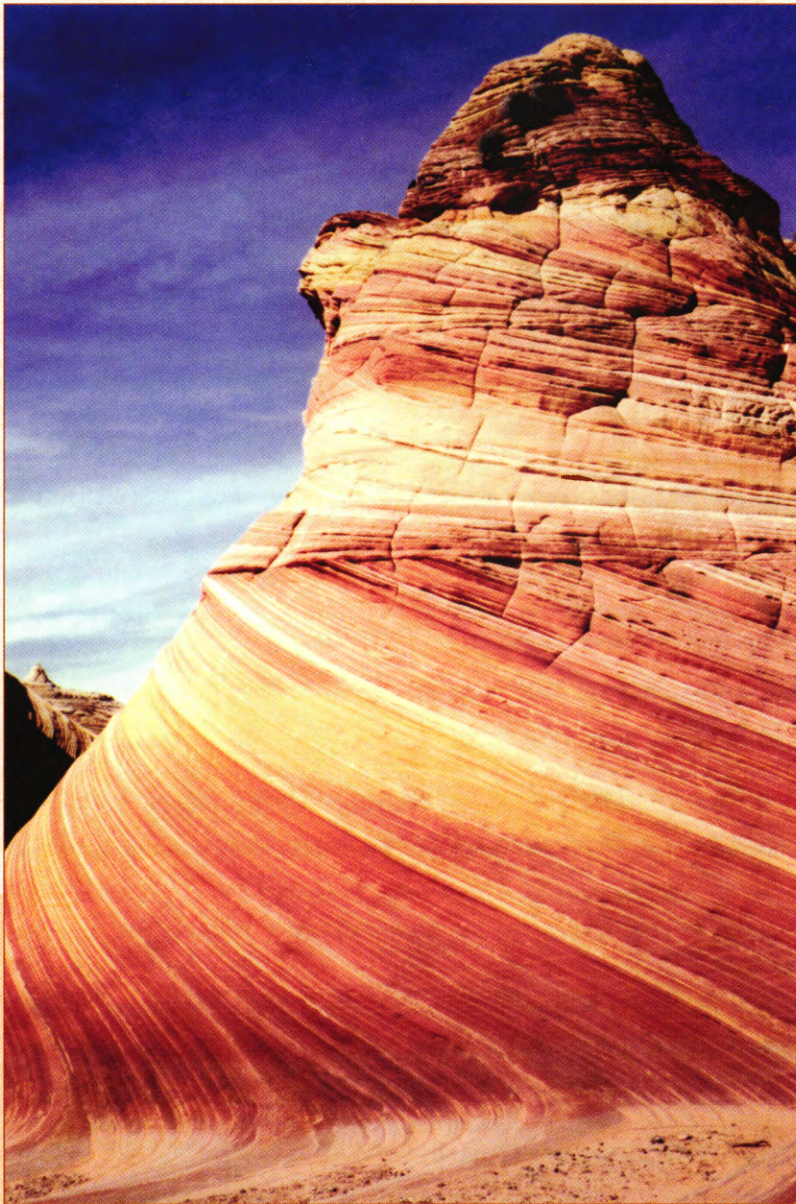
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*Rainbow of colors in the Navajo Sandstone, Coyote Buttes - Paria Wilderness Area,
Utah-Arizona border.*



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