DINOSAURS UP CLOSE

The photographs shown with these articles are somewhat magnified cross-sectional views of silicified dinosaur bone, mineral shadows of ancient beasts that roamed the floodplains and low hills of western Colorado and eastern Utah 150 million years ago. I hope they capture some presence of those ancient creatures as well as the beauty of the naturally colored agates that now entomb and preserve them. Agatized dinosaur bone of this quality was never easy to come by, and although I collected dinosaur bone slabs for decades, it was many years before I began to examine them under bright light and low-power magnification. I was amazed at what I found: a world of brilliant colors and subtle, delicate agate floats and banding I'd never suspected. The moods were astonishingly varied in this small world, from light, almost humorous motifs that reminded me of Paul Klee paintings to somber and evocative tapestries, explosions of brilliant, vibrant color, and subtle, tweedy textures and weaves. Here are the paisleys of the mineral world, complex cloisonnés in stone, marbled colors and mineral sunsets, each bone uniquely recorded in its crystalline remains, frozen here into intricate and evocative images. Strikingly beautiful and suggestive as compositions, these remnants of former life evoke ancient creatures that have suffered an earth change “into something rich and strange,” and to further paraphrase Shakespeare, “these are jewels that were their bones.”

Uplifted in relatively recent times, erosion has now exposed these bones, and gravity slowly pulls them down into gullies and canyons. Weathered, completely fragmented and scattered, the hard bone chunks remain behind on the surface as many dozens of feet of surrounding clay wash from around them. In time this accumulation becomes a 'surface enrichment' of bone debris. These photographs are all from such broken and scattered material, mostly collected in the 1950s and ‘60s when rockhounds with jeeps first got interested in the colorful, scattered pieces of bone then often found on soft Morrison Formation bentonitic clays. Most of these surface accumulations have by now been well picked over, and while slabs and specimens continue to be cut, mostly from old stock, the most colorful material, never common, has become increasingly scarce.

Some preservationists argue that these scraps of bone, though usually of no paleontological value, should have been left in place for others to enjoy (and that the same is true for arrowheads and old pot shards). But it was a different era back then and a different mind-frame prevailed. I found a young *Brontosaurus* in my early teens (The Smithsonian was not interested in my site), and we all collected pot shards and arrowheads. For the most part this still strikes me as an interesting and pretty harmless hobby. Yet I know of ranchers who destroyed Anasazi ruins to find pots and burials (or sometimes did so just to prevent the government from telling them what they could or could not do with their land), and others who crudely bulldozed bone beds to get what they wanted. In the ‘80s

I heard of an entrepreneur who'd bought several tons of scrap bone and then ran it through a mining ball mill grinder in the hope of creating uniform pieces that could be wrapped in cellophane to make cereal box "prizes." Apparently bone doesn't break up into nice, uniform little chunks, so he salvaged the remains by using it as dino-gravel for his muddy driveway.

My father, a geologist, wrote an article in the late '50s for Scientific American Magazine's 'The Amateur Scientist' recommending bone-hunting on public land as an enjoyable family activity, though of course the assumption was that any valuable find would be turned over to the experts, and I know, and know of, a number of rockhounds in western Colorado in the '60s and '70s who did just that. Nonetheless, a few offenders are all it takes to spoil the game, so vertebrate fossils and Anasazi discards are now off-limits on public land.

GEOLOGY

The dinosaurs whose bones house these agates lived in a landscape now represented by fluvial sediments and beds of gray-green shale known as the Morrison Formation ("Morrison"). This famous formation is found on the surface from southern Montana to New Mexico and Arizona, and in Colorado east to the Great Plains, where it disappears under younger sediments. Core samples reveal its presence at depth under western Nebraska, the Dakotas, and into southern Canada. A large, contemporary depositional basin of the same type might be the Pantanal, adjacent to the Paraguay River in Brazil and eastern Bolivia, or perhaps the nearby Gran Chaco plain (Dodson et al., 211). Estimates vary as to how long this low-lying basin of rivers and ponds lasted. Some suggest it was substantially intact for five or ten million years (Foster, 38; Dodson et al., 220).

These photographs are from bones found in eastern Utah and western Colorado. Bones from the Morrison in this area are usually associated with clays, sands and gravels indicating former river channels, but they're also found in lakebeds and in badlands of colorful bentonitic clays. Bentonitic soil is a chemically modified (hydrolyzed) volcanic ash rich in silica and metal hydroxides and oxides. The relatively soluble silicates, dissolved in groundwater, in time silicify the bone, and the metal hydroxides-oxides create bright colors when present in even very small amounts.

Morrison sediments were likely deposited by intermittent, shifting streams under seasonally wet but normally semi-arid conditions. (Hallan, as cited in Hintz, 50) The Morrison landscape was home to many of our most familiar dinosaurs, including *Allosaurus, Brontosaurus, Diplodocus, Brachiosaurus, Camarasaurus*, *Stegosaurus*, and *Barosaurus*, as well as more than a dozen lesser known species. In these photographs you are looking at some of these great beasts up close.

BONE PETRIFICATION

Let's take a look at how these dinosaur bones became the fossils you see in these photographs.

For a dinosaur bone to become an agatized fossil the bone must be buried in a wet environment where collagen (a structural protein) and other organics that bind the bone's calcium phosphate platelets can be broken down by bacteria, then dissolved and washed away by groundwater. The bone gets weaker as it decays, opens up in places, and may or may not be crushed under the weight of sediment. Gravels wash into the larger spaces, silt finds its way into distant openings, and clay minerals may, in time, precipitate into even the most remote recesses. With water comes the progenitor of the silicates, soluble silicic acid. These molecules diffuse into even the most remote micropores. In time a complex polymeric silicic gel is formed, and from this, much, much later, after going through several configurations, microcrystalline agate precipitates. Or so most experts propose; more on this later.

The mineral in most fossilized bone from the Colorado and Utah Morrison is typically a fluorine and carbonate rich variety of apatite (a group of calcium hydroxyl phosphate minerals) called francolite, a close relative of the carbonate hydroxyapatite crystallites in living bone (Hubert et al., 535-539). Living bone is primarily a calcium phosphate, but once buried, the original bone crystallites adapt to their new chemical environment by incorporating other ions dissolved in groundwater, principally fluoride, along with trace minerals. These minerals are usually either black or brown, sometimes yellowish, and they reveal the bone’s original structure in great detail. The sometimes brilliant displays of colored agate form in spaces once filled with fatty marrow and other living tissue within the bone’s medullary core.

Bone structures are of two basic types, one a relatively dense outer bone and the other a spongy, inner bone made up of many little linked, freeform rods called “trabecular struts.” The outer “cortical” bone supports and strengthens and so has few openings in which agate might form, other than the small haversian canals that once held blood vessels and nerve fibers. But the inner “cancellous” bone is an open work of trabeculae once surrounded by marrow, which provides ideal openings for the formation of agate. Sometimes, in a bone that had decayed or been eaten or fractured, large open spaces were created that eventually filled with agate.

What we think of as living “bone” (the hard stuff) is actually a composite tissue of collagen interwoven with orderly arrangements of sub-microscopic crystals of carbonate hydroxyapatite. The body constantly draws on the bones’ mineral wealth to sustain its chemical needs. For example, nerve impulses are carried by calcium ions, and these, when needed, may be drawn in part from the calcium in bone crystallites. Mineral mass is constantly being added to bone for growth and strength, and drawn from it to sustain the chemical needs of the body. This close association of hard, brittle, crystalline mineral and pliable collagen allows living bone to give support while also offering resilience and flexibility.

Initial petrification is believed to take place during or shortly after the collagen has been decomposed by bacteria and groundwater. Microbial action plays an important part in this decay, but groundwater alone can react with the large protein molecules in collagen and break them into polypeptides and amino acids, which are both smaller and more water soluble than the original material (Hare, 212).

Although I've seen slabs of bone so thoroughly silicified that the absorbed trabecular struts have become "ghosts"—dark, diffuse strands in translucent agate—in most cases the decaying dinosaur bone keeps its original hydroxyapatite crystallite fine structure. The prevalent view today is that bone mineral remains in most fossil dinosaur bone (Hubert et al., p.531). "Diagenesis" is alteration of rock and their constituent minerals at near earth-surface temperatures and pressures, which includes fossilization. In fossil bone a transformed hydroxyapatite crystallite (francolite) grows slowly until it and similar crystals fill the surrounding micro-spaces that once held collagen.(Hubert et al., p.542). This growth may increase the crystal's size by a factor of ten or more, but its orientation usually remains unchanged (Chure, D., pers. comm.). Fortunately the high carbonate alkalinity of the regional groundwater helps preserve these crystals, which dissolve rapidly at a pH below 6. Later silicification of open spaces in the bone may give francolite further protection (Hubert, p.545), though other authors rely on the permeability of cryptocrystalline quartz to facilitate silica deposition.

Though silicic acid concentrated in groundwater may have already formed an initial coating of amorphous silicon dioxide on the bone, this gel or low-order opaline material is permeable to small molecules. Thus there's a long period in which organic materials can break down, become more soluble, and leach out through the silica deposition. This of course allows space for further silica and francolite deposition, and as these chemical reactions are happening simultaneously, it's possible that protein breakdown and migration may have some chemical role in promoting these reactions (Leo and Barghoorn, 20). I've personally collected small concretions whose centers were occupied by chips of dinosaur bone (or very rarely, a tooth), an obvious case of petrogenesis controlled by organic compounds. It's also believed that bacteria or their chemical remains, together with chemicals from the dead body and surrounding rock, may provide the geochemical environment necessary for the formation of some silicates (Pewkliang et al, 141; Jacka, 427) by mediating and facilitating certain reactions and by providing nuclei that facilitate polymerization (the reaction of monomer molecules to form more complex polymer chains or three-dimensional networks) followed by mineral precipitation.

The center of a large bone may be hollow (at least among Theropod dinosaurs) and a cavity is created in any large bone if its cancellous component breaks up. These large areas can fill with banded agate and crystalline quartz, often with a calcite center. Specimens like this can be interesting and beautiful display pieces and very splashy when seen from a distance. But the pictures here come from the bone's interior or from the area that lies between a bone's core and its outer cortex, the area of spongy bone structures called cancellous bone, an open network of interconnected bone struts with lots of surrounding space that agate can fill.

AGATE FORMATION

One hundred and fifty million years ago when the Late Jurassic Morrison Formation was slowly being deposited on flood plains in what is now western Colorado and eastern Utah, exciting events were happening far to the west, where a tectonic plate subducting beneath North America created a chain of volcanoes whose deep granitic roots are today's Sierra Nevada. The deformation also promoted volcanism in Nevada, Idaho and northwestern Utah (Stokes, l20; Schweichert et al. in Hintze, 99).

Volcanic ash is the secret ingredient in our fossil story. It provided much of the soluble silica from which agates formed and it supplied the metal hydroxides and oxides that colored them. Ash is common in the Morrison, blown in from the west and then reworked by stream sediments. Its porosity and open chemical structure (it's mostly an amorphous, molecularly disorganized volcanic glass) provided a continuous supply of silica. Ash beds are dissolved with relative ease by rain and groundwater and are thus the source of highly silicified bone and wood deposits worldwide (Leo and Barghoorn, 26). The many ash beds in the Morrison are major contributors to the bentonitic shale "badlands" which often contain well-silicified dinosaur bones and from which comes the most colorful agatized material. The specimens shown in these photographs are from surface 'float' collected in such areas. Weathered and fractured, the harder bone chunks remained behind on the surface as many dozens of feet of surrounding clay washed from around them. As a result it's usually impossible to know which dinosaur a given fragment came from, though by the same token it's good to know that nothing of scientific value was lost in collecting these fragmented and scattered debris.

Bright color in agate and jasper is usually derived from iron hydroxides and oxides, sometimes oxides of manganese, occasionally oxides of cobalt or copper, all these and more plentifully supplied by volcanic ash. They can color agate at very low concentrations, a few percent to a small fraction of a percent by weight (Smithsonian Exhibit; Leo and Barghoorn, 8), but if too plentiful will produce muted or dark colors. Most Morrison bone is rather plain looking, usually muddy browns and grays or greenish tans and blacks, often crumbly and highly fractured, sometimes with too much ugly calcite and not much silicate. Every once in a while pieces are found with the beautiful colors you see in these photographs, but only if the right conditions existed, conditions that may have varied widely over time. A structure once created—whether macroscopic or molecular—can be restructured or removed under new conditions. Agate itself is colorless, and in most locations the many minerals we find unattractive are usually the ones that color it, and these typically dominate the more colorful ones.

How does the agate form?

Although it's easy to write conventional chemical equations that look plausible and show required reaction products (Verhoogen et al., 310), in point of fact silica geochemistry is often extremely complex at the smallest scales. Specific reaction products involving different forms of silica depend on many intricate physicochemical interactions including silica activity, porewater and groundwater chemistry, crystal nucleation, colloidal silica, surface area, chemical reaction kinetics (which includes a dozen and more variables), microbial populations, changing acidity and carbonate alkalinity, and diagenesis, including elevated temperatures and pressures. For example, parts of the Morrison Formation may have been deeply buried—perhaps 2000^{+}m—during the Laramide Orogeny (Woldegabriel and Hagan, 21). Additionally there are thermodynamic factors such as chemical equilibrium states and free-energy relationships, so it all gets rather complicated.

Even when mineral structures and properties can be observed, caution must be exercised when predicting the evolution of these chemical systems (especially ones that may take millions of years to form reaction products such as agate) because they frequently depend on subtle and imperfectly understood factors (Verhoogen et al., 69). Chemical and structural formations in agates are often poised at the edge of criticality, with many outcomes possible and many subtle factors collectively pushing reactions this way or that. As an analogy, the formation of clouds and weather exhibit a similar complexity, with outcomes dependent on chance and a host of ever-changing variables. As complexity theorist Stuart Kauffman put it, "History arises when the space of possibilities is too large by far for the actual to exhaust the possible" (186).

Agate cannot be made under laboratory conditions, and even if it could be, Nature might have achieved the same result in many different ways. Although there's some general agreement on a basic outline of agate development, there's also much disagreement on details, even major ones, despite many serious efforts to understand its origin.

Some few believe that agate can be formed directly, and quickly, from silica-rich solutions (Heaney, "How Do Agates Form?"; Campos-Venuti, 140, 159), but most believe that millions if not tens of millions of years are necessary (Felix, as cited in Buurman, 5; Leo and Barghoorn,11-12), and the end-point, crystalline quartz (clear quartz), though thermodynamically preferred, may never form.

Note that quartz crystals can form directly under some conditions and are occasionally found in the center cavities of long bones and in small, tight mosaic clusters in cancellous openings. Macrocrystalline quartz can form only when the influx of silicates slows or when polymerization has diluted any remaining water.

The silica solute that dissolves most easily in groundwater (especially in more alkaline waters) is (ortho)silicic acid ($Si(OH)_4$) (Buurman, p.5). Each molecule contains a silicon atom surrounded by four hydroxyl (OH) groups.

These independent monomers then link together loosely to form complex polymeric molecules, with amorphous silica likely to control dissolved silica concentrations above quartz saturation because it is more reactive (Longmire, pers. comm.). A diffuse colloidal fluid forms initially, but as polymerization progresses this solidifies and a large, amorphous macromolecule forms that in time, with increasing cross-linkage, becomes a true gel. These links form by condensation: Two OH groups join to create an oxygen bond between two silicon atoms while creating a new H_2O molecule in the process. These silica colloids and gels are permeable both to small molecules moving outward and to additional silicic acid molecules moving inward within the bone.

Silica deposition continues as a self-perpetuating system; the removal of dissolved silicic acid molecules by polymerization creates a local deficit in adjacent porewater and groundwater that is replenished through diffusion (thermal molecular motion in the liquid environment) from areas of higher silica concentration. A molecular conveyor belt is thus established, driven by diffusion itself, new silica atoms brought into depleted areas even in the absence of substantial interior water movement. Diffusion of silicic acid in bone can take place over distances of centimeters to decimeters over thousands and millions of years (Longmire, pers. comm.). It’s likely that in cracked and broken bones there will be openings where silicic acid can be transported by the complex flow paths of groundwater movement or changes in the water table, which simplifies the task of diffusion.

Chemical systems are lazy at heart and, like many other physical systems, try to avoid tension by finding the maximum relaxed (stable) equilibrium among the forces in that system. For minerals this “relaxation pathway” means seeking a crystalline arrangement, the lowest energy conformation at a given temperature and pressure.

To satisfy thermodynamics' requirements, these molecules in time evolve through a series of polymorphs that show increasing crystallinity, their atomic arrangement thus increasingly regular and periodic (Pewkliang et al., 140; Hesse, 255). The end-state of this series is monocrystalline quartz with its tight crystal lattice, clear and hard, almost insoluble in water, and with atoms as densely packed as silica tetrahedrons can be at ambient temperatures and pressures. These polymorphs begin with the aforementioned amorphous silica, which in time becomes a gel, followed by opal, a hydrated silica. This opal, initially amorphous opal (Opal-A, Opal-AN, Opal-AG), then begins to show signs of increasing crystalline order. Opal-CT is semi-crystalline and Opal-C even more so.

Next in this series is a progressive change toward the fibrous microcrystalline (“cryptocrystalline”) quartz called chalcedony, which includes agate, jasper and flint. In agates, chains of oxygen and silicon cluster into helical, roughly parallel fibers that are visible under polarized light and which usually radiate from nucleating centers on the surrounding bone (Hesse, 258). Geometry dictates that the further the fiber bundles grow from their initial nucleating points the more they will appear as bands (Akhavan, The Quartz Page). Other explanations for banding have been proposed: Is it a form of Liesegang banding, the still poorly understood geochemical self-organization found in some rocks and as a lab experiment in silicic acid gels (among others)? Are they the result of changing physical and chemical conditions, of relatively rapid variations in crystallinity, pH and water content (Campos-Venuti, 117-118)? Something else?

Observation suggests that when viscous, many interesting phenomena can occur in some agates: growth of chemical “gardens,” pendulous “stalactites,” various dendritic forms and more. If these grow in large enough cavities and are heavy enough, growths like these may slide, slump, drip, bend and fold.

The majority position holds that agates form over millions, if not many tens of millions of years, during which time a silicic-gel filled (or largely filled) cavity obeys thermodynamics' rules by slowly progressing through a series of molecular re-arrangements. Each rearrangement has more molecular order until, if given enough time, it transforms itself, atom by atom, into clear quartz crystals. These theories propose massive self-reorganization of the original silicic-gel (as do several theories of agate banding).

A minority of mineralogists claim that under some conditions agates can form in the course of decades, with banding a reflection of seasonal changes in rainfall and a water table that repeatedly withdraws, triggering dehydration and silica deposition (though “hardening” may take substantially longer)(Campos-Venuti, 115-145).

“Four economists, five opinions,” as the saying goes, and all of them persuasive. Theories on agate formation are numerous and often contradictory. I've read a dozen and more technical papers on agate formation over the years, all interesting, all persuasive.

It's perhaps understandable that smart people have reached so many different conclusions, but also enjoyable that some mysteries linger on. I wish the researchers and theoreticians success, but would not be displeased if the puzzle of agate formation remains perplexing and unresolved for a while yet. For me an agate's charm and beauty reside at least in part in the mysteries of its form and formation.

I once found classic root cross-sections in an otherwise ugly slab of bone, a story from long ago about plants growing in swampy terrain where a large beast had died not long before. The discovery made me feel unusually close to these ancient creatures and the world they inhabited. All these bones, colorful or not, are tokens of the distant past, exciting rocks that once lived and breathed and walked upon the earth, as we ourselves do in our brief turn.

A note on the photography: These photographs of naturally colored bone were taken with Kodachrome 25 slide film in reflected, unfiltered, non-polarized white light. The image ratios on the original 35mm film range from about 2:1 to 3:1, which appears to the eye as a ten-power magnification, roughly. These images were chosen from perhaps 500 photographs of some 200 slabs and polished fragments. Images copyright 2018 by Cress Kearny.

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