

MINERALS MATTER

Apatite: Following the movements of ancient humans and mastodons

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Apatite is a mineral that gives structure to bones and teeth, and can be used to determine where you have traveled based on what you have eaten—apatite records your appetite! Apatite is the most abundant mineral in your body and is composed primarily of calcium (Ca) and phosphate (PO₄) [as Ca₅(PO₄)₃(F,OH)] that are bound together in a rigid crystalline framework (Fig. 1). Joined together with collagen (your body’s most abundant protein), tiny apatite crystals provide the stiffness in bones that support your body and the hardness in teeth that allow you to eat tough foods. One reason that we find fossil skeletons of dinosaurs today is because they contain apatite, which is readily preserved for millions of years.

But apatite is more than just a strong mineral. The ability for elements to substitute in trace quantities for calcium (Ca) and hydroxyl (OH) in apatite (Fig. 1) can provide paleontologists and archeologists with a life-long record of body chemistry. Trace amounts of the element strontium (Sr) provide a special tool for tracking ancient animal movements through analysis of the ratio of two different strontium isotopes (also see the “Nitty Gritty Details” box)—⁸⁷Sr and ⁸⁶Sr. So, how does this work? Geochemically, “you are what you eat,” meaning that your body’s chemistry, including the apatite in your skeleton, reflects the composition of the food you eat and water you drink. The food and water that you consume contain trace amounts of Sr. And the two flavors of Sr, ⁸⁷Sr vs. ⁸⁶Sr, occur in different amounts, depending upon the local geology and soils in which plants grow. So plants absorb Sr (and other elements), animals eat plants, and then humans eat plants and animals, which all happen to contain lots of Sr. The ratio of ⁸⁷Sr to ⁸⁶Sr (symbolized by ⁸⁷Sr/⁸⁶Sr¹) depends on rock type: old igneous and metamorphic rocks have high ⁸⁷Sr/⁸⁶Sr (meaning there is more of the ⁸⁷Sr isotope relative to ⁸⁶Sr), whereas limestones and young volcanic rocks have low ⁸⁷Sr/⁸⁶Sr. So, if an animal moves around during its lifetime, say between areas underlain by limestone vs. old granite, where food and water ⁸⁷Sr/⁸⁶Sr values are different, the animal’s ⁸⁷Sr/⁸⁶Sr ratio will change correspondingly and be recorded in its apatite. These differences, captured in tiny samples of apatite, can be easily measured by a mass spectrometer.

Archeologists use these types of Sr isotope changes in bioapatite to reveal ancient human movements. The key here is that different tissues, such as the bioapatite in bones and teeth, grow and match sequential changes in chemistry that occur at different times, much in the same manner that tree rings, for example, grow at different times. So by analyzing different tissues, and knowing when they equilibrate with the body, an isotopic history of location relative to soil with different ⁸⁷Sr/⁸⁶Sr can be developed. A famous application involves “Ötzi,” a mummified ~46 year-old man who lived about

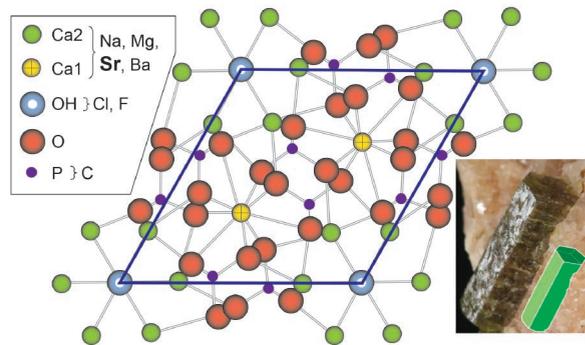


FIGURE 1. Atomic arrangement of apatite, showing locations of calcium (Ca1 and Ca2 sites), hydroxyl (OH), phosphorus (P), and oxygen (O). Legend shows common elemental substitutions. Notice that Sr, as well as Mg, Na, and Ba, can substitute for Ca. Image and sketch of apatite crystal from a marble from Canada illustrate apatite crystal symmetry.

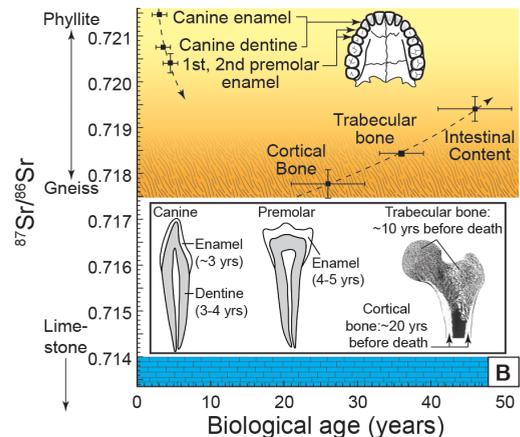
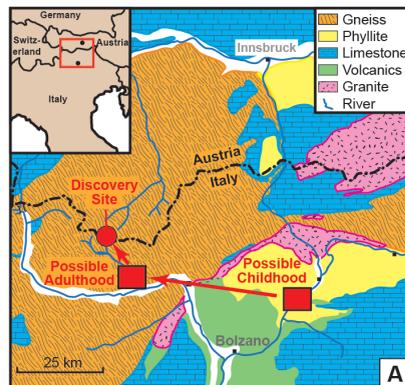


FIGURE 2. Location of Ötzi, a ~5000 year old mummy in the Alps and Sr isotope data that help identify where he lived as a child and as an adult. (a) Different rock types in the region and possible locations where Ötzi lived, based on Sr isotope data. (b) Sr isotope data for materials that record different times in Ötzi’s life: different teeth (childhood), different types of bone (adult), and stomach contents (just prior to death). Values of ⁸⁷Sr/⁸⁶Sr discriminate limestone (low ⁸⁷Sr/⁸⁶Sr) from gneiss and phyllite (high ⁸⁷Sr/⁸⁶Sr). Colors correspond with rock types in a. Insets show cross sections of teeth and bone, and timing of growth (teeth) or recrystallization (bone).

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Nitty Gritty Details:

Isotopes: Isotopes refer to the different masses of the atoms of an element. The nucleus of a specific element always contains the same number of protons, equal to its atomic number, but it can contain a different number of neutrons. For example, all Sr atoms contain 38 protons, but the four natural varieties can contain 46, 48, 49, or 50 neutrons, making the four isotopes, ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr . The superscripts represent the number of protons (38) plus the number of neutrons (46, 48, etc.). The ratio $^{87}\text{Sr}/^{86}\text{Sr}$ (“Strontium eighty-seven–eighty-six”) is commonly used as a tracer of rock age or type.

Why we use $^{87}\text{Sr}/^{86}\text{Sr}$: Although four isotopes of Sr are stable, so do not radioactively decay, the slow decay of radioactive ^{87}Rb makes extra ^{87}Sr . Therefore, rocks can develop a high $^{87}\text{Sr}/^{86}\text{Sr}$ if they are old (lots of time for ^{87}Rb to decay), and/or have high Rb contents (shales and granites or their metamorphic equivalents—phyllites, schists, and gneisses have high Rb). Rocks can have low $^{87}\text{Sr}/^{86}\text{Sr}$ if they have low Rb, such as limestones and/or basalts, or if they have high Rb are very young. Analyzing $^{87}\text{Sr}/^{86}\text{Sr}$ allows us to discriminate whether an animal got its food and water from an area whose bedrock was old metamorphic and igneous rocks (high $^{87}\text{Sr}/^{86}\text{Sr}$) vs. young sedimentary rocks (low $^{87}\text{Sr}/^{86}\text{Sr}$).

Mass spectrometer: A mass spectrometer is a modern analytical instrument that separates atoms with different masses and allows us to measure the amount of ^{87}Sr and ^{86}Sr in a material.

Mastodon or Mammoth?: Both are members of the order *Proboscidea*, which included many different species in the past, but now is populated solely by elephants. Mastodons had lumpy teeth and ate a lot of leaves and twigs. Mammoths had banded teeth and preferred eating grass. Both became extinct at the end of the last Ice Age.

5000 years ago in the central European Alps (Müller et al. 2003). Analysis of his teeth, bones, and intestinal contents reveal that he generally lived within ~60 km of the discovery site, along Alpine valleys to the south that are underlain by old metamorphic rocks, known as gneisses and phyllites. But he also moved around within that area (Fig. 2). Such analyses provide clues about the prehistoric lifestyle of the only human we have found from that time.

Another study involved Sr isotope zoning within a fossilized mastodon tooth from Florida, which revealed annual migration patterns of these elephant cousins (Fig. 2; Hoppe et al. 1999). These patterns would have been impossible to figure out any other way. A key observation is that teeth form from top to bottom (Fig. 2b), and in large herbivores teeth require more than one year to reach their maximum size. So by measuring such growth zoning in teeth, we can identify where an animal lived seasonally, sometimes over multiple years. Zoning in the Mastadon tooth (Fig. 3) shows that this individual mostly lived in areas with moderate $^{87}\text{Sr}/^{86}\text{Sr}$, but occasionally migrated to areas with lower and higher $^{87}\text{Sr}/^{86}\text{Sr}$. Local geologic variations in $^{87}\text{Sr}/^{86}\text{Sr}$ show that these animals must have migrated at least 100 km each year, and perhaps more than 500 km.

Apatite’s ability to record the geochemistry of past diets provides an important way to study the life history of humans and other animals long after death. This information helps us evaluate hypotheses about how human cultures evolved, and how ecosystems functioned in the past.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation grant EAR-1349749. Thanks to Steve Shirey for initiating this project, teachers Tanya Gordon and Julie Ekhoﬀ for comments on an early version, and Dave Mogk, Holly Godsey, and Alex Speer for reviews.

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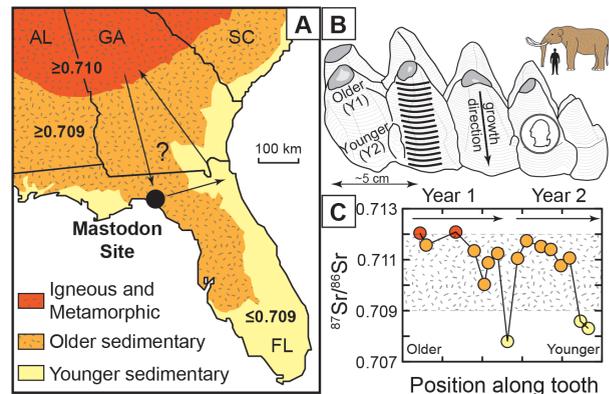


FIGURE 3. Results of study of Hoppe et al. (1999). Colors correspond with rock types. (a) Southeastern US, showing regions of higher (dark red) vs. lower (light yellow) $^{87}\text{Sr}/^{86}\text{Sr}$. (b) Sketch of mastodon lower molar tooth, showing shape, growth direction of a single cusp, and typical sampling strategy used in other studies (black bands, representing the tracks of a drill; Hoppe et al. 1999 used a somewhat different approach based on the same principles). US quarter (similar in size to a euro) for scale. Gray areas on top of five cusps are facets produced by grinding against opposing molars. Inset compares size of mastodon vs. human. (c) Sr isotope zoning in mastodon tooth showing that this animal must have migrated seasonally in the region, possibly as indicated by arrows. Rise in $^{87}\text{Sr}/^{86}\text{Sr}$ represents movement to regions underlain by igneous and metamorphic rocks, and dip in $^{87}\text{Sr}/^{86}\text{Sr}$ represents movement to regions underlain by younger sedimentary rocks.

See also:

- [1] Elements, June 2015, vol. 11, no. 3: Apatite: A Mineral for All Seasons.
 [2] Lithographic Monograph no. 17: Apatite—The Great Pretender, <http://www.minsocam.org/msa/Lithographie/#Apatite>.

Endnote:

This is an inaugural article in a series entitled “Mineral Matters”. These 2-page articles are written in a newsy style and targeted toward high-school science students, illustrating how a natural mineral species can be used in fundamental research in Earth science.