Dating of moon samples: Pitfalls and paradoxes

The movement of volatilized metals over the surface of the moon could be confusing interpretations of the ages of lunar samples

by Everly Driscoll

The earth's moon represents one chapter and key to the origin and evolution of the solar system and perhaps the universe. Compared with the earth's surface, which has been largely eroded, the moon is an open history book with four-billion-year-old rocks lying around on its surface. The problem is to interpret that book accurately. That, more or less, has been the rationale and problem for lunar exploration.

Trying to unravel lunar history by long distance, or even by sampling six or seven areas of the surface, is a precarious job and subject to much interpretation. Much controversy during the past two years has centered around the interpretation that should be given to the ages of the lunar material—ages yielded by studying its radioactive history. If all of the age-dating methods (rubidium-strontium, uranium-lead and potassium-argon) had yielded the same ages, the picture would be neat. But they haven't. The lead ages, for example, have been consistently older.

This led Leon T. Silver of the California Institute of Technology to study the temperatures at which lead volatilizes (vaporizes) and moves out of the lunar sample. Theoretically, this could happen on the moon and this volatilized lead would become "parentless"—separated from its uranium parent. More lead (parentless lead added to the material) would yield older ages. This problem opens up the whole question of volatilization of metals in the lunar vacuum during the moon's early history. When this question is fully understood it may have direct bearing on the present and future use of the reservoirs of metals on earth. Silver's work along with similar work being done by Mitsonubu Tatsumoto and Bruce Doe of the U.S. Geological Survey in Denver is bound to be the topic of some controversy at the upcoming 3rd Lunar Science Conference in Houston, Jan. 10 to 13.

Lunar scientists reconstruct the chronology of the moon's past by various methods: crater counting (older areas have more craters); ray analyses (ejecta from older craters are not as bright and most often are covered up by subsequent ejecta from younger craters); particle-track-counting (solar wind, solar flare and cosmic ray particles that bombard the moon's surface leave radiation tracks: the more tracks, the longer the material has been on or near the surface); and by chemical and mineral analyses (different compositions represent different processes and events). But all of these methods are relative.

The rate of radioactive decay provides a relatively fixed point (age) on which to construct subsequent or earlier events. Isotopic ages have been obtained for material from five landing sites on the moon—those of Apollos 11, 12, 14, 15 and Luna 16; each site has a different age. But in a given site, the ages also vary, indicating that more than one event has occurred. Ideally, however, any one basaltic rock from a given site should yield the same isotopic age, regardless of the method used.

Each radioactive isotope has a fixed rate of decay called a half-life—the time in which about 50 percent of the material would have decayed into another isotope. For example, by counting the atoms of the radioactive parent, uranium 238, and the atoms of its radiogenic daughter, lead 206, lunar scientists can determine how long the uranium has been in that material. (The more daughter-atoms relative to the parent atoms, the older the sample.) Theoretically, if there are as many lead atoms as uranium atoms—assuming all the lead daughters present are derived from the parent present—the age should be 4.5 billion years (the half-life of uranium 238).

Rubidium 87 has a half-life of 50 billion years and decays into radiogenic strontium 87. (However, some strontium 87 exists naturally—not as a result of rubidium 87 decay.)

In addition to uranium 238 converting to lead 206, uranium 235, with a half-life of 713 million years, decays to form lead 207, and thorium 232, with a half-life of 14 billion years, decays to form lead 208.

What complicates things for the uranium-lead method is that nonradiogenic lead 204, 206, 207 and 208 also exist naturally, and scientists are not sure what the ratios of nonradiogenic to radiogenic lead were early in the moon's history. Wherever there is nonradiogenic lead 204, however, there is usually nonradiogenic lead 206, 207 and 208. To arrive at the percentage of nonradiogenic lead present on the early moon, one can take the ratios of nonradiogenic lead 206 to 204, 207 to 204 and 208 to 204 found in meteorites (these ratios are 9.5, 10.5 and 20, respectively); but the question unanswered is, are these meteoritic lead ratios the same as those that existed on the moon? Those scientists who are willing to accept the 4.6-billion-year-old age of meteorites and apply that to the moon are often not willing to apply the lead ratios found in meteorites to the moon.

Basalts (a common type of igneous, extrusive rock) are the easiest to date. The assumption is that the radioactive parent present in the rock was fractionated from all of its daughters prior to crystallization in the basalt. Thus the number of daughter atoms present now indicates how long the parent had been isolated in the rock from its previous other daughters and had been decaying to produce the new daughters there—or when it crystallized.

Breccias—rocks that have a metamorphic past—are another story. One rock may have several different ages. Lunar rock 12013 is assembled of materials with rubidium-strontium ages averaging 4.5 billion years, but the whole rock was subjected to a significant metamorphic recrystallization about 4 billion years ago.

The "Genesis Rock" of Apollo 15's Hadley Rille site has an apparent potassium-argon age of 4.15 billion years (SN: 9/25/71, p. 203). Basalts from

Mare Putredinis at Hadley Rille date 3.3 billion years by the rubidium-strontium method. The breccias and basalts from Apollo 14's Fra Mauro date 3.9 billion years by the rubidium-strontium method (SN: 7/3/71, p. 5), and 4.2 billion years by the uranium-lead method. The basalts of Apollo 11's Mare Tranquillitatis date 3.6 billion years by rubidium-strontium and 4.1 to 4.2 by the uranium-lead. Basalts from Apollo 12's Oceanus Procellarum date 3.3 billion years by rubidium-strontium and 3.95 to 4.15 by uranium-lead. The largest chunk (62 milligrams) of Luna 16's Mare Fecunditatis material dated by the rubidium-strontium method has an age of 3.4 billion years.

But the most puzzling data so far from the age dating by all three methods have been the apparent ages of the soil from all of the sites—ranging from 4.2 to 4.9 billion years—considerably older on the average than the ages for the rocks. How could the rocks be younger than the soil? Lunar scientists have sought several explanations. One is that some magic ingredient such as KREEP (material with high concentrations of potassium, uranium, thorium, rare earth elements and phosphorus) from the highlands has been mixed in with the soil (SN: 1/23/71, p. 61). Another is that perhaps the rocks were depleted in radioactive isotopes before the rocks crystallized. And a third is that perhaps the soil has incorporated meteoritic material from impacting bodies.

The other major question is why does the uranium-lead method yield older ages—both in the rocks and in the soil—than the rubidium-strontium method?

Caltech

Silver: Lead may hold history key.

The early impulse was to accept unquestioningly the rubidium-strontium ages and sort of sweep under the rug the apparent differences yielded by the uranium and potassium methods. The age discrepancies have been under intensive study since the Apollo 11 returns, and at Caltech, Silver now thinks he is getting some answers.

The findings are telling scientists as much about lunar processes and the behavior of volatiles in a vacuum as about the ages of the moon.

The presence of large amounts of basaltic glass on the moon indicates a rather extensive thermal history from volcanic or impact events or both that generated temperatures as high as 1,100 to 1,200 degrees C. (melting temperature of basaltic rocks) and higher. These events have obviously affected the materials, such as lead, strontium and potassium, scientists are now studying.

Using soil samples from Apollos 11, 12 and 14, Silver first separated out the radioactive components by acid wasting (leaching or rinsing the surfaces). He then sized out the different particles and volatilized them in a partial vacuum.

The result, says Silver, is that he can volatilize out of a sample of lunar soil both radioactive parents and radiogenic daughters. About 50 percent of the lead became volatilized in one hour at 970 degrees C. Silver estimates that 75 percent of the lead could be moved at this temperature in 20 hours. Even more significant was that at temperatures as low as 550 degrees C., he volatilized 3 to 11 percent of the lead in one hour. By separating material 36 microns and smaller from the larger stuff, Silver found a 200-million-year shift in the apparent age of the Apollo 11 soil. This is significant because the finer the material, the easier and farther it would travel over the lunar surface.

Lead within rocks volatilized at 980 degrees C.; rubidium, at 980 degrees C.—well below the high temperatures believed to be present in the early history of the moon. "In the experiment with lead," says Silver, "most of the variation in the ages of the samples can be explained by merely adding or subtracting volatile lead. If indeed parents and daughters are moving about on the lunar surface this way, this could be confusing the interpretation of the ages."

"Parentless lead," as he calls it, would be those atoms which do not belong to the uranium parent present in the lunar material. When daughters, such as lead 206, are added through volatilization, the net result is to increase the apparent age of the soil. If parents such as rubidium have been added to the soil more recently than the time of the formation of the rock components in the soil, the age of the rock would be interpreted to be younger. And, says Silver, "If we are moving lead by vapor transfer, we are moving other elements as well—not only gases, but volatile metals.

"Anytime there had been a lava lake on the moon, that would have been an optimum condition for boiling volatile metals into the lunar vacuum. Further, any great impact that would be reflected in a large crater could move metals because of the temperatures generated by the impact." (The metal atoms move out of the samples and into the lunar vacuum and then back onto the surface. "These things have long free paths," says Silver. "They will move around until they hit something: There is no interference [as on the earth] by atmospheric atoms." It is difficult to incorporate the lead back into the minerals. It just stays on the surface in the soil, or on the rocks. It is also difficult to boil lead off the moon.)

For these reasons, says Silver, volatile lead may have the best long-term memory of the early history of the moon. "It may permit us to look back at earlier stages of the moon than any other method." How can this happen?

Lead is an important tracer because, unlike strontium and argon, lead has more than one radioactive parent. Each of them—thorium 232, uranium 238 and uranium 235—decays at a different rate (the half-lives are 14 billion, 4.5 billion, and 713 million years respectively). The ratios of parents to daughters and different daughters to other daughters change with greater sensitivity with time, and this sensitivity increases as one goes back in time.

An example of lead's "memory" can be illustrated by the results of an Apollo 11 sample. Assuming a basaltic rock from Mare Tranquillitatis was formed 4.6 billion years ago, the uranium in it would produce daughters until something happened to that rock. The rubidium-strontium ages say that something happened at that site 3.6 billion years ago. What then could have happened is that some of the lead daughters in the rock volatilized at that time, but not all of them. But after the event, the uranium began producing other daughters. Thus the older daughters (those produced from 4.6 to 3.6) become mixed in with the younger daughters (produced from 3.6 to the present). When the rocks from Apollo 11 were dated, they all gave an apparent uranium-lead age of 4.1. The unexplainable fact is that not one, but all of the rocks from the site had a 4.1 age, which means that the lead had to be boiled off in all of the rocks at a fixed rate. This, says Silver, should not have happened, especially when one assumes that all the rocks would not have had the same ratios to start with. What was expected was that the ratios of lead would be spread out—say from 3.6 to 4.6 billion years, but they weren't. Why is not yet understood.

Another example is with sample 14163. This sample, says Silver, has already shown that some parts of the lead could not have formed more recently than 4 billion years ago, and it probably includes some components considerably older than 4.0 billion years. Silver heated the sample. At 550 degrees C. the lead that came off had very high lead 207 to 206 ratios. One would have expected to see a ratio of 0.6 lead 207 to 206 for lead that had been forming continuously since 4.5 billion years ago. But what he saw were ratios of 1.2 or 1.3. "This isotopic composition has never been observed anywhere in the material of the solar system," says Silver. If these lead ratios were interpreted as other ratios, the lead would have apparent ages as high as 5.5 billion years. But, says Silver, "We are probably looking at lead 207 made very early in the solar system before it could be diluted with lead 206, and this large amount of lead 207 has had more time to move around." Lead that is similarly bound comes off at the same temperatures. There is usually a correlation with the age of the lead, but the implications of this are not fully understood.

Tatsumoto and Doe have been working with lead at different temperatures (1,000 to 1,350 degrees C.), and they are getting similar results. The most significant has been isolating lead that consistently dates at 4.6 billion years old (SN: 12/18/71, p. 423).

The problem of how much lead was around to begin with still remains. This could be partially solved by dating all of the soil samples from the moon, determining the over-all effects on each soil sample and getting a convergence point.

The broader implications of the history of volatile metals are apparent even if not all of the results and answers are yet. Volatile metals such as mercury, lead, zinc, cadmium, bismuth, rubidium and potassium are important to man. If scientists could unlock the history of these chemical reservoirs—what the chemical pot started from, how it evolved and what makes it work—says Silver, and if they could understand these processes on the moon, they might know how to use them today on earth and predict for tomorrow. "We don't know the total chemistry of the earth, but our best chance of understanding it is on the moon." □

Taking proteins apart

Living cells take proteins apart and reuse their amino acids. Research is beginning to probe the mechanisms of the process.

by Dietrick E. Thomsen

Living cells continually synthesize proteins from amino acids and continually take proteins apart. In healthy tissues the mass of protein inside the cells is kept in equilibrium by a balance between synthesis on the one hand and degradation and secretion on the other.

The synthesizing part of this cycle is a fashionable topic for biochemical investigation today, but, says J. Ken McDonald of the National Aeronautics and Space Administration's Ames Research Center, "the effort being expended on the investigation of intracellular protein degradation is barely perceptible by comparison."

Yet the degradation process is as important as synthesis. It involves, as McDonald puts it, the recycling of used proteins for the formation of new ones. One instance in which its role may even be predominant is the atrophy of tissue. The most visible example of atrophy is the shrinkage of muscles in a limb that is disused, because of paralysis or for some other possible reason. But there are other possibilities. The condition of weightlessness, to which astronauts are subject, may induce disuse atrophy in

NASA Ames Research Center

McDonald: Recycling used proteins.

skeletal and heart muscles, bone and cartilage. Atrophy may result from a decreased rate of synthesis, an increased rate of degradation or a combination.

Proteins and polypeptides consist of long chains in which the individual units are various amino acids. The route of degradation from protein to single amino acids involves a series of steps in which the compounds are broken into smaller and smaller pieces. The breaking occurs under the chemical influence of certain enzymes, and study of the action of these proteolytic enzymes is expected to lead to an understanding of the intracellular degradation process.

Proteolytic enzymes not only accomplish the recycling of proteins, they also produce substances with important physiological effects.

For example, in certain cases of physiological stress a particular proteolytic enzyme normally present in blood plasma in an inactive state releases a peptide called bradykinin from a plasma globulin. Bradykinin is one of the most potent agents known for dilating blood vessels and lowering blood pressure; it is believed to be instrumental in producing shock. A converse to bradykinin is angiotensin, which raises the blood pressure. Angiotensin is also formed in the blood, and requires the action of proteolytic enzymes from both kidney and lung. Once their intended physiological effects have been produced, these polypeptides, in their turn, are degraded to inactive substances by yet other proteolytic enzymes.

A third reason to study proteolytic enzymes is that they can degrade hormones such as growth hormone, adrenocorticotrophic hormone (ACTH), parathyroid hormone, thyrocalcitonin, vasopressin and insulin into inactive substances. All these are polypeptides, or small proteins. Certain of these hormones—for example growth hormone and thyrocalcitonin—may perform significant actions offsetting detrimental atrophic changes that occur during weightlessness. If they do, it would be important to know how their activities could be regulated.