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Hot Idea

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The Growing Diversity of Lunar Basalts

--- A lunar basaltic meteorite adds complexity to the already complicated story of mare basalt volcanism on the Moon.

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Lars Borg (Lawrence Livermore National Laboratory, LLNL) and colleagues at LLNL, the University of New Mexico, the University of California, Berkeley, and Arizona State University have made detailed measurements of trace elements and isotopes in Northwest Africa (NWA) 032, a lunar basaltic meteorite. Previous studies had already shown that the rock is a low-titanium mare basalt. Among other things, Borg and coworkers determined the isotopic compositions of strontium (Sr), rubidium (Rb), samarium (Sm), and neodymium (Nd) present in the rock when it crystallized. The abundances of these elements and their initial isotopic ratios reflect the chemical characteristics of the region of the lunar interior where the NWA 032 magma formed.

Borg and his colleagues found that this place in the lunar mantle (called "mantle source area") is quite different from the places where other lunar mare basalts formed. The Rb-Sr data indicate that the mantle source has higher concentrations of incompatible trace elements (they concentrate in magma, not in the major minerals making up planetary interiors) than do the source regions of other low-Ti mare basalts. On the other hand, the Sm-Nd data suggest that the concentrations of incompatible trace elements are lower than in other mare basalts. This mysterious conflicting evidence sets NWA 032 aside from other mare basalts. Geochemical modeling leads Borg and colleagues to conclude that three factors led to the unique chemical characteristics of the NWA 032 mantle source area. One is that it does not contain any "urKREEP," the last dregs of crystallization of the lunar magma ocean, the vast globe-encircling magma body that existed when the Moon formed. The second is that it does not seem to contain any plagioclase, whereas other mare basalt source regions did contain this mineral. The third factor is that the NWA 032 magma probably formed by much smaller amounts of partial melting than did other basalts, 2% versus 5-10% for other lunar basalts. The more samples we get, the more we learn about the Moon.

Reference:

• Borg, L. E., Gaffney, A. M., Shearer, C. K., DePaolo, D. J., Hutcheon, I. D., Owens, T. L., Ramon, E., and Brennecka, G. (2009) Mechanisms for Incompatible-element Enrichment on the Moon Deduced from the Lunar Basaltic Meteorite Northwest Africa 032. *Geochimica et Cosmochimica Acta*, v. 73, p. 3963-3980.

PSRDpresents: The Growing Diversity of Lunar Basalts--<u>Short Slide Summary</u> (with accompanying notes).

From the Lava Plains of the Moon

Northwest Africa (NWA) 032 was first described in a massive paper by Tim Fagan (Univ. of Hawai'i, now at Tokyo Institute of Technology) and a bunch of co-authors (including one named Bunch). Lars Borg and his colleagues use that work as a basis for their study.

NWA 032 is a volcanic rock. We can readily see this from its texture, the way crystals are intergrown. As seen in the element map below, NWA 032 contains larger (up to 0.3 mm across) crystals of the minerals olivine and pyroxene set in a much finer-grained matrix of pyroxene, plagioclase, ilmenite, and assorted other minerals. The matrix (also called groundmass) has a texture indicative of rapidly-cooled lava. Besides the igneous minerals, NWA 032 also has weathering products--not from the Moon, but from northwest Africa. They consist of mostly calcium carbonate and a smaller amount of calcium sulfate.



Lunar Basaltic Meteorite NWA 032

(From Fagan et al., 2002, Meteoritics & Planet. Sci., v. 37, p. 371-394.)

Element map produced with an electron microprobe of an entire thin section of NWA 032. Colors correspond to the intensity of K-alpha X-ray spectral lines from aluminum (red), iron (green), and silicon (blue). This allows us to readily identify large crystals of olivine (green) and pyroxene (blue), with smaller crystals of pyroxene (slightly lighter blue than the larger pyroxene grains) and plagioclase (reddish). The dark cracks are filled with minerals produced by terrestrial weathering, mainly calcium carbonate (calcite), which does not contain the mapped elements, so the cracks are dark in this image. The terrestrial weathering products are one of the analytical problems Lars Borg and his colleagues had to deal with in making their isotopic measurements of the rock.



(From Fagan et al., 2002, Meteoritics & Planet. Sci., v. 37, p. 371-394.)

Feathery intergrowth of elongate pyroxene (light gray) and plagioclase (dark gray) crystals. Logically enough, petrologists call this a "plumose" texture. Experiments on lunar basalt compositions indicate that this texture forms when lava cools at about 20 to 60 degrees Celsius per hour.

The minerals in NWA 032 have a wide range in chemical composition, shown especially by the relative amounts of iron and magnesium in olivine and pyroxenes. This is shown in the image below, which shows relatively large, roughly square-shaped crystals of olivine and pyroxene with bright rims on the olivine. The rims are much richer in iron than are the crystal interiors. Smaller pyroxene crystals have a range of brightness, indicating a range in iron/magnesium. (This grayscale difference arises because the image is of electrons scattered off the surface of the sample, and the amount of scattering is proportional to the average atomic number of the material under the electron beam. Iron has a higher atomic number than does magnesium, so higher iron means more electrons backscattered, hence a brighter color.)

Phenocrysts in NWA 032

(From Fagan et al., 2002, Meteoritics & Planet. Sci., v. 37, p. 371-394.)

Large olivine (Olv) and pyroxene (Pyx) crystals are suspended in a much finer-grained groundmass of pyroxene, plagioclase, and ilmenite (plus some minor phases). The larger crystals have bright rims, which indicate in this backscattered electron image that they are richer in iron than are the interiors. Pyroxene even has a subtle change in color inside the large grains (marked by arrows), indicating a change in composition. The pyroxene in the matrix is all brighter than the interiors of the large pyroxene grains. Note the boundary between the olivine at the top center and the pyroxene next to it (with labels). There is no bright, iron-rich rim on either, indicating that the two crystals formed simultaneously. Black, elongate grains in the matrix are plagioclase crystals. White grains in the matrix are mostly ilmenite, an iron-titanium oxide.

The blocky shape and the sizes of the large olivine crystals allowed Fagan and coworkers to place limits on the rate at which the lava was cooling as the olivine crystallized. Based on experiments done during the 1970s in the experimental petrology laboratory at the Johnson Space Center, the shapes of the olivine indicate that the olivine crystals grew in a lava cooling slower than about 2 $^{\circ}$ C/hour. Fagan assessed assorted parameters that affect the rates at which minerals grow and calculated that it took between 3.5 and 35 days for the largest olivine crystals to grow to the sizes observed. Thus, it took days or a month for the big crystals to form, but the texture of the matrix indicates much faster cooling. Again calling on experiments done in the 1970s at the Johnson Space Center, Fagan compared the texture of the matrix of NWA 032 to experiments done on experimental magmas with the composition of low-Ti mare basalt. The best match to the texture was when the cooling rate was 20 to 60 $^{\circ}$ C/hour, about 10 times faster than required to grow the larger, square olivine and pyroxene crystals.

Putting all these data on cooling rates together, Fagan and his coworkers conclude that the magma in which NWA 032 formed cooled slowly at first, probably in the volcanic conduit that delivered it to the surface. When the lava erupted, it was no longer insulated by surrounding rock, so it began to cool rapidly. Lava flows are complicated, dynamic bodies, so it is impossible to say if the volume of lava from which NWA 032 formed was close to the surface (maybe meter or two), or broke out from a lava flow as is common in pahoehoe lava flows on Earth. Details aside, it is clear that the lava cooled slowly at first, then rapidly.

So, NWA 032 is a volcanic rock, but how do we know it comes from the Moon? Many lines of evidence point definitively to a lunar origin. The two most important ones are:

- Its oxygen isotopic composition is exactly on the line defined by samples from the Earth and Moon. We can rule out the Earth because NWA 032 contains small grains of metallic iron, instead of the presence of ferric iron in at least some minerals in terrestrial basalts. The Earth-Moon proportion of oxygen isotopes is different from other meteorite samples, except for one type: enstatite chondrites and achondrites. However, the enstatite meteorites contain essentially no ferrous iron in their silicate minerals, a stark contrast to NWA 032, which contains lots (for example, olivine contains at least 33 wt% FeO).
- 2. The Fe/Mn (iron/manganese) weight ratio is useful for distinguishing among assorted solar system materials. The differences result from a combination of processes in the solar nebula, especially the relative volatilities of iron and manganese, and those inside asteroids or larger bodies, such as how oxidizing the interiors are. For bulk-rock analyses, the Fe/Mn ratio among Apollo samples is in the range 65 to 80; NWA 032 has Fe/Mn of 69.8. Cosmochemists can also test for parent body origin by measuring the amounts of iron and manganese in olivine and pyroxene, as shown in the diagrams below. The data straddle the Moon line and show a clear distinction between NWA 032 and either Martian meteorites or the HED meteorites, which are thought to come from asteroid 4 Vesta.



Concentrations of Fe and Mn in olivine (left) and pyroxene (right) in NWA 032. The lines were defined in a paper by Jim Papike (University of New Mexico). The unusual concentration units express Fe and Mn in terms of the chemical formulae of olivine and pyroxene. In establishing the lines on the diagram, Jim Papike used these mineralogically-based units because they relate to each mineral's crystal structure, and in part because he's a crystallographer and that's just the way crystallographers are.

Different from Basalts from Other Maria

NWA 032 has chemical characteristics that set it apart from most other basalts from the lunar maria. Fagan and his cohorts showed that NWA 032 has distinctive trace element concentrations; this result is now confirmed by additional analyses by Borg and his team. An example is shown in the diagram below, which plots thorium/hafnium against titanium/samarium. These are not randomly-chosen element ratios. The behavior of the four elements during melting of the lunar interior and by reaction with other rocks as the magmas migrate to the surface tend to separate these elements from one another, making them useful as geochemical fingerprints.

The important observation is that NWA 032 plots far from where the Apollo mare basalts plot (the fields labeled

"High-Ti" and "Low-Ti"). In fact, NWA 032 plots near the point labeled "urKREEP," the hypothetical chemical component thought to be the final product from the lunar magma ocean, the globe-encircling magma body that existed when the Moon formed. Nearby that point and NWA 032 are a point for KREEP basalt 15386 (a different kind of lunar basalt) and two other lunar basaltic meteorites, NWA 773 and LAP 02205 (from the LaPaz ice field, Antarctica). Borg and coworkers point out that NWA 032, LAP 02205, and NWA 773 seem to be related to KREEP. They note that this could mean KREEP infiltrated parts of the lunar interior, causing magmas produced there by partial melting to have the KREEP trace-element signature. Alternatively, a magma produced in a lunar interior free of KREEP might have assimilated some KREEP from the upper mantle or lower crust on its way to the surface. Either way, the magmas end up with KREEP chemical characteristics. Borg also notes another alternative. The NWA 032 magma might have been produced by smaller percentages of partial melting. The isotopic data could distinguish among these alternatives.



This plot of element ratios separates the samples and shows potential links to KREEP, which is high in trace elements. Only rocks for which isotopic data for rubidium-strontium (Rb-Sr) and samarium-neodymium (Sm-Nd) are plotted. NWA 032 and a couple of other lunar basaltic meteorites plot near the point labeled urKREEP, suggesting that the portion of the mantle in which they formed was enriched in trace elements or that the magmas reacted with KREEP before erupting. An alternative is that the NWA 032 magma formed by very small amount of melting in the lunar mantle. Lars Borg and his colleagues measured the isotopic compositions of Rb, Sr, Sm,

and Nd to test these two hypotheses.

Painstaking Isotopic Analyses

Whenever I read a paper about detailed isotopic studies of any rock, I thank my lucky shooting stars that I did not fall under the complicated spell of the isotope witch, trapped in a world of clean rooms, mineral separates, ion exchange columns, and complicated lab chemistry, rather than looking at rocks in microscopes of one sort or another. This is especially true for extraterrestrial rocks because they might have been shocked and heated by impacts or weathered while sitting around on the Earth waiting to be found.

Lars Borg's work on NWA 032 is another example of heroic, painstaking work. One obstacle is that the rock is generally too fine-grained to allow separates of individual minerals. Instead, the rock was crushed to a powder between 44 and 75 micrometers in size and fed through a Frantz Isodynamic Magnetic Separator. This device is mostly a large electromagnet with a metal trough running through it. Cosmochemists use this to separate mineral

mixtures into batches of powder enriched in one mineral, a necessary step for the isotopic studies, by varying the strength of the magnetic field or the slope of the trough. It works because minerals differ in their magnetic properties.

The trouble with most meteorites that are found on Earth (rather than observed to fall) is that they can suffer the same weathering processes as any terrestrial rock does. Water can react with the meteorite, changing its composition a little or a lot, or it can flow into cracks and evaporate, leaving behind a residue of terrestrial stuff. The terrestrial products can greatly alter isotopic and other chemical observations. Fortunately, NWA 032 is not too weathered, but it does have cracks that contain carbonate and sulfate minerals deposited from terrestrial water. To rid the samples of the interloper minerals, Lars Borg plopped the magnetic separates in ultra pure hydrochloric acid. Twice--once at 25 °C in an ultrasonic bath for 10 minutes and a second time on a hot plate at 45 °C for 15 minutes. This produced a bunch of samples: magnetic separates obtained at different settings of the magnetic separator, the residues of the leaching and the accompanying leaching solutions, plus two samples not run through the magnetic separator (but leached), and two hand-picked olivine-rich samples. To see an impressive flow chart of this procedure and of the samples produced, <u>click here</u>.

Geochemical Diversity of the Lunar Interior

The Rb-Sr and Sm-Nd isotope data define straight lines in the two diagrams below, giving the same age by each technique, about 2.9 billion years (within analytical uncertainties): 2947 ± 16 million years for Rb-Sr and 2931 ± 92 million years for Sm-Nd,. This age is among the youngest ages determined on samples of mare basalts, although crater counting shows that some mare basalt flow fields are as young as a billion years. Two other lunar meteorites also contain young mare basalts, NWA 773 and LAP 02205, both close to 3.0 billion years old.



(From Borg et al., 2009, Geochim. et Cosmochim. Acta, v. 73, p. 3963-3980.)

Data for the leaching residues from NWA 032 (black dots) fall on lines in the Rb-Sr (left) and Sm-Nd (right) diagrams. Such lines are called "isochrons" and their slopes define the age when coupled with the rate of radioactive decay of either rubidium-87 or samarium-147. Discerning readers are no doubt wondering about the open circles, almost all of which lie off the lines. Does this Borg guy cherry-pick the data? Certainly not. The open circles are the solutions produced when the samples were leached to remove terrestrial weathering products. The filled circles show isotopic compositions for the magnetic separates or whole-rock samples from which the terrestrial weathering materials were removed. These magnetic residues are free of environmental contamination in northwest Africa, and so they record the age of crystallization of the basalt on the Moon.

Possibly more important than the age of the rock are the value of the y-axis intercepts of the isochrons. These are the initial isotopic compositions of the regions in the lunar mantle at the time the magma formed. As shown in the diagram below, there is a spread in the initial Sr and Nd isotopic compositions among lunar basalts, which indicates significant variation in the composition of the lunar interior. (The neodymium initial ratios are converted to epsilon units, which compares the initial Nd isotopic composition to the initial solar system values as given by chondrites.) The calculated mantle source for NWA 032 has a higher Rb/Sr ratio than other mare basalt samples, but is lower than the sources for KREEP basalts. The Nd isotopes show the reverse: NWA 032 is significantly higher than the sources calculated for KREEP basalts. Borg and his colleagues conclude that this disparity indicates that there is a fundamental difference in the processes that produced the NWA 032 mantle source than those that operated during formation of the sources for other mare basalts.



Plot of basalt eruption age versus initial Sr (top, a) and Nd (bottom, b) isotopic compositions. The lines are calculations that show how the isotopic compositions changed with time. The calculation for Sr assumes that the Moon formed 4.558 billion years ago and that the Moon began with a strontium-87/strontium-86 ratio of 0.69903. For Nd, the calculation assumes that there was a two-stage process: a chondritic isotopic ratio evolves from lunar origin until 4.42 billion years ago, and then follows different paths. The calculations are guides for how the isotopic compositions changed with time for different Rb/Sr or Sm/Nd ratios.

What are the differences between the NWA 032 source region and those where the other mare basalts formed? To answer this question, Borg and his colleagues made extensive geochemical calculations to test different models for producing the observed initial Sr and Nd isotopic compositions. They conclude that one important difference is that the NWA 032 source region did not contain any plagioclase feldspar, whereas the source regions for typical mare basalts contain a few percent plagioclase. The NWA 032 source region also did not

contain a significant amount of urKREEP, a chemical component formed near the end of crystallization of the lunar magma ocean, and common to most other mare basalts. NWA 032 is relatively rich in the trace elements, such as the rare earth elements, that characterize KREEP, so why is it not there? Borg and colleagues argue that NWA 032 formed by much smaller percentages of partial melting inside the Moon--the smaller the amount of melting, the higher the concentration of many trace elements in the magma. Small amounts of melting accentuate differences in how elements partition between the unmelted mantle rock and the magma, giving rise to differences between Rb/Sr and Sm/Nd.

More Samples, More Knowledge

The detailed research done on NWA 032 and other lunar meteorites highlights the importance of obtaining additional samples of the Moon. Many chemical features of NWA 032 distinguish it from mare basalts collected by the Apollo program and reveal that the lunar interior differs chemically and mineralogically from place to place. Similarly, Randy Korotev (Washington University in St. Louis) has documented that meteorites from the lunar highlands differ significantly from those collected by the Apollo missions, all to the nearside. Although we do not know where a specific meteorite comes from on the Moon, half of them must come from the farside. Thus, Korotev's observations suggest that the farside highlands and perhaps the underlying farside mantle are geochemically different from the nearside highlands. The Moon is physically and chemically lopsided.

To continue to understand the diversity of the lunar surface and interior, hence to understand its bulk chemical composition and origin, we need more samples. The meteorites will continue to enlighten, but samples from known locations will be particularly valuable because we can put them into the overall geochemical context provided by global remote sensing data. Of course, retrieving samples is complicated, but certainly possible--in the early to mid-1970s, the Soviet Union flew three unpiloted, sample-return missions, Luna 16, 20, and 24. Lunar scientists have identified numerous sites on the Moon where a simple sample-return mission (grab samples, no rover needed) will enhance our knowledge of the Moon and its geological history.



http://www.zarya.info/Diaries/Luna/Luna24.php

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- **PSRDpresents:** The Growing Diversity of Lunar Basalts--<u>Short Slide Summary</u> (with accompanying notes).
- Borg, L. E., Gaffney, A. M., Shearer, C. K., DePaolo, D. J., Hutcheon, I. D., Owens, T. L., Ramon, E., and Brennecka, G. (2009) Mechanisms for Incompatible-element Enrichment on the Moon Deduced from the Lunar Basaltic Meteorite Northwest Africa 032. *Geochimica et Cosmochimica Acta*, v. 73, p. 3963-3980.
- Fagan, T. J., Taylor, G. J., Keil, K., Bunch, T. E., Wittke, J. H., Korotev, R. L., Jolliff, B. L., Gillis, J. J., Haskin, L. A., Jarosewich, E., Clayton, R. N., Mayeda, T. K., Fernandes, V. A., Burgess, R., Turner, G., Eugster, O., and Lorenzetti, S. (2002) Northwest Africa 032: Product of Lunar Volcanism. *Meteoritics and Planetary Science*, v. 37, p. 371-394.
- Korotev R. L. (2005) Lunar Geochemistry as Told by Lunar Meteorites. *Chemie der Erde*, v. 65, p. 297-346.
- Papike, J. J., Ryder G., and Shearer, C. K. (1998) Lunar Samples, in *Planetary Materials* (ed. J. J. Papike), p. 5-1 to 5-234. Reviews in Mineralogy, v. 36, Mineralogical Society of America, Washington, D. C.



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