

energies no higher than 20 eV—were emitted as much as 700 attoseconds later, as seen in figure 2. That's sluggish relative to theoretical predictions, especially in the lower portion of the kinetic energy range that was measured.

When electrons meet

Valence electrons are critical for molecular reactions, but the study of core electrons can reveal other processes. On their way out of a molecule, ionized core electrons can interact with the more weakly bound valence electrons. In fact, the researchers' numerical simulations show that some of the core electrons' delay, plotted in figure 2, may be caused by interactions with valence electrons.

Once it's emitted from its shell, a core electron, unlike a valence electron, is quickly replaced by an electron in a higher-energy orbital farther from the nucleus. Through a process known as Auger–Meitner decay, the energy released when a core vacancy is filled gets transferred to a valence electron, which is then emitted from the molecule after a few femtoseconds.

"Collisions with Auger electrons have not been observed before in photoemission delay experiments," says Kevin Prince, a senior scientist at the Elettra Sincrotrone Trieste research center in Italy. "Multielectron scattering is also new in this context."

Theoretical models have struggled to accurately predict photoemission delay at the lowest electron kinetic energies; figure 2 illustrates the discrepancy between measurements and simulations. The unexpectedly long photoemission delay in the new measurements indicates that core electrons may be more sensitive to multielectron interactions than previously thought. The team has started conducting new XFEL measurements on more complex molecules, which should provide even more information about the unique interactions of core electrons.

Alex Lopatka

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Three glass beads bring into question the timeline of lunar volcanism

Radiometric dating of material returned from the Moon suggests there was active volcanism on the satellite 120 million years ago, nearly 2 billion years more recent than previous estimates.

China's *Chang'e 5* mission brought samples of the Moon back to Earth in December 2020, the first time since the Apollo and Luna missions did so in the 1970s. The next year, the lunar science community was rocked by the finding that volcanic basalts in the new samples were some 2 billion years old,^{1,2} about 800 million years younger than any other measured lunar volcanic rocks.³ Just as theorists were developing models of the Moon's thermal evolution that could explain that finding, Bi-Wen Wang, of the Chinese Academy of Sciences in Beijing, and colleagues are now reporting dramatically younger ages of around 120 million years.⁴

The new age measurements are from 3 glass beads, shown in figure 1, out of a sample of roughly 3000 collected by the *Chang'e 5* probe. Most of the beads have impact origins: When meteorites smash into the lunar surface, small blobs of melted material get thrown upward before cooling and falling to the ground. But glass beads can also be generated by volcanic sprays known as lava fountains. Lunar soils returned by the Apollo missions contained many such beads, all older than 3 billion years.

Although this is the first direct measurement of volcanic material from the Moon to indicate sub-billion-year-old

ages, the idea of more recent volcanism isn't totally new. Detailed analyses of lunar surface images have revealed dozens of small volcanic features (see figure 2) known as irregular mare patches (see the article by Brett Denevi, *PHYSICS TODAY*, June 2017, page 38). The density of impact craters can be used to appraise the age of a lunar surface. That method has yielded estimates that the largest patches could be less than 100 million years old, but there have been no direct measurements to confirm those assessments.⁵

The latest finding has generated a lot of buzz in the lunar science community. Still, not everyone is convinced that the three beads are conclusively volcanic. The University of Florida's Stephen Elardo, who works on thermal evolution models of the Moon, says explaining the latest finding would require going back to the drawing board. "If there's young volcanism on the Moon, we really need to rethink models about how planets cool off with time," he says. "And that isn't just the Moon, that goes for any planetary bodies."

Winnowing candidates

The Moon is thought to have formed after a collision between Earth and a protoplanet early in our solar system's formation, about 4.5 billion years ago

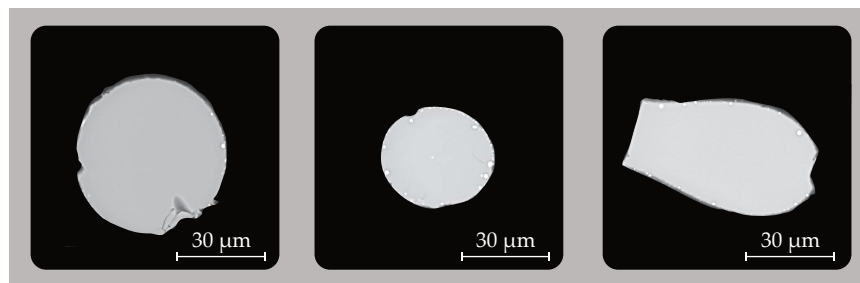


FIGURE 1. BACKSCATTERED ELECTRON IMAGES were used to screen for fractures and compositional variations in glass beads collected by the *Chang'e 5* mission. Three beads from a sample of 3000 were identified as volcanic in origin and found to be 2 billion years younger than any other volcanic material from the Moon. (Adapted from ref. 4.)

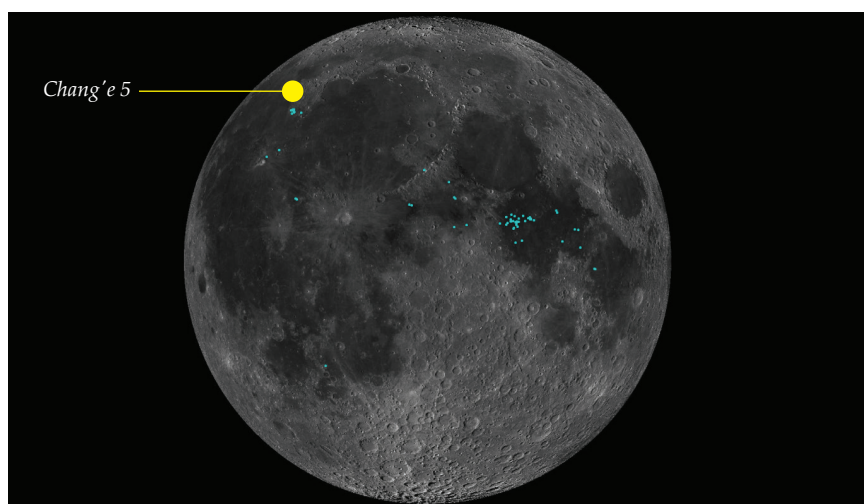


FIGURE 2. THE MOON'S NEAR SIDE was visited by *Chang'e 5* in December 2020. Lunar features known as irregular mare patches, labeled with blue dots, have been interpreted as younger volcanoes that could be the source of the geologically young glass beads found in the return samples from the Chinese mission. (Image adapted from Lunar QuickMap.)

(see the article by Dave Stevenson, *PHYSICS TODAY*, November 2014, page 32). Starting from a fully molten state, the lunar magma ocean crystallized into a core, mantle, and crust. Many interacting processes, including magma differentiation, crystallization, mechanical overturning, and mantle convection, produced the variety of rocks and features observed on the Moon's surface today. The oldest rocks reside in the highlands that cover much of the lunar far side. The younger rocks are found in large low plains of dark basalts, known as lunar maria, that cover much of the near side. The landing site of *Chang'e 5* was chosen to target an area expected, based on crater counts, to be on the younger end of lunar basalts.

Wang and colleagues followed multiple steps to identify potentially volcanic beads from the *Chang'e 5* sample. First, they used backscattered electron imaging to screen out beads with obvious signs of impact origins, such as fractures and highly variable compositions. The remaining beads were analyzed for major elements like magnesium, calcium, and aluminum. They used the relative proportions of those elements to separate the beads by origin: either likely volcanic or likely impact. Data from the Apollo missions provided a baseline for classification. That process winnowed the candidates for beads of volcanic origin down to 13.

A radiometric age can be obtained from a bead by comparing the ratio of

uranium-238 in the bead with its decay product, lead-206. But volcanic beads that experienced a meteorite impact after they formed could have uranium-lead ages that were thermally reset, since the heat of an impact would have kicked lead out of the sample. To be sure that the 13 beads with volcanic compositions weren't thermally reset, the researchers turned to sulfur isotopes. Regolith from the Moon's surface typically exhibits a higher ratio of sulfur-34 to sulfur-32 compared with a standard reference material from Earth. But volcanic glass beads from the Apollo missions have more sulfur-32, which gives them a lower sulfur-34 isotope ratio, as seen in figure 3.

With the sulfur data from their glass beads, Wang and colleagues make the case that impacts cause degassing from rocks that preferentially kick out light sulfur-32: As total sulfur concentration decreases, the amount of sulfur-34 increases relative to sulfur-32.

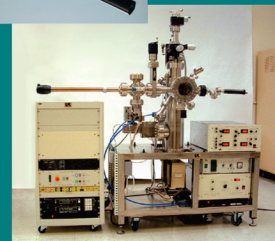
The researchers found that 10 of the 13 beads have a heavy sulfur isotope signature and thus ruled them out as purely volcanic in origin. The remaining three are enriched in lighter sulfur isotopes. From that, the team concludes that the three beads are volcanically sourced and would provide reliable ages. The researchers also argue that high levels of rubidium found in those samples, and not in the impact beads, further rule out a resetting of the uranium decay clock because the heat needed to

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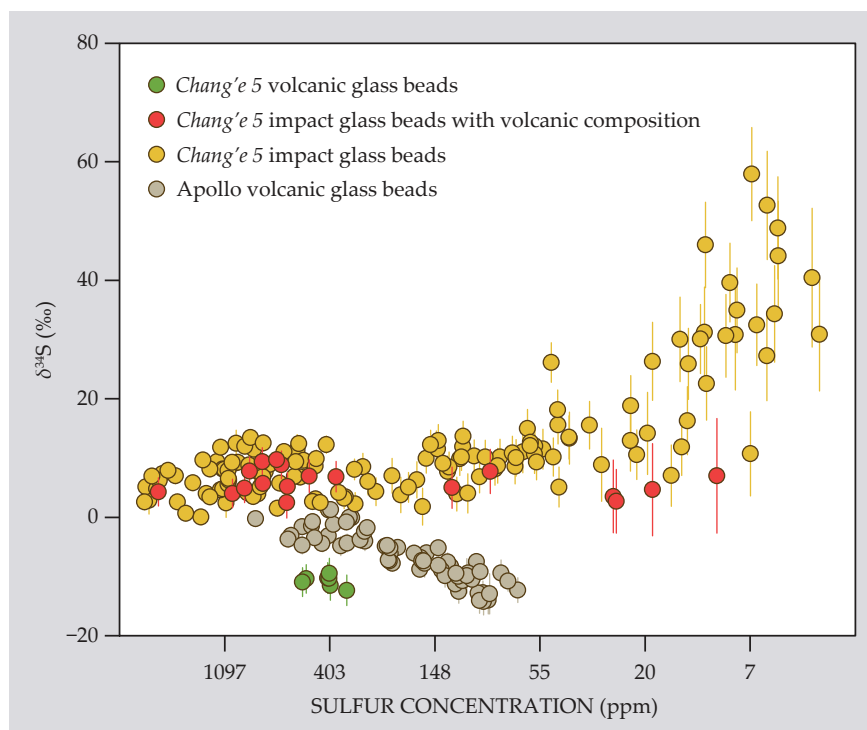


FIGURE 3. SULFUR ISOTOPES measured from lunar glass beads, shown here as a relative ratio of sulfur-34 to sulfur-32 compared to a standard reference from Earth, may help distinguish beads generated by lava fountains from those made during meteor impacts. Out of 13 glass beads with compositions that seemed volcanic in origin (red and green) from the *Chang'e 5* sample, researchers determined that only three beads (green) had sulfur isotope ratios similar to volcanic glass beads collected during Apollo missions (gray). (Adapted from ref. 4.)

kick lead out of the glass would also kick out rubidium. Uranium–lead dating shows the ages of the three beads all clustered around 120 million years.

“Such young volcanoes on the Moon have been expected by remote sensing observations, but we found the ground truth,” says Qiu-Li Li, who led the research team.

Wang and colleagues did not measure the ages of any glass beads that they deemed impact related. But a previous study of hundreds of such beads from the *Chang'e 5* samples found that the ages spanned from a few million years to more than 2 billion years old,⁶ without the clustering around 120 million years that Wang and his team report for their volcanic beads.

Brown University’s James Dottin III, who has studied sulfur isotopes in lunar glass beads, says he agrees that impacts cause sulfur loss, but his own work has shown that impacts don’t cause sulfur isotope fractionation.⁷ He doesn’t see proof of a strong fractionation trend from the *Chang'e 5* sulfur

isotope data and notes that it’s hard to get reliable data on sulfur concentrations below 10 ppm.

Dottin argues that the separation and concentration of sulfur in lunar glass beads has more complex origins. “Just because the sulfur isotope ratio is negative doesn’t mean it’s volcanic,” he says. He would have liked to have seen images of the samples after the collection of measurements from secondary ion mass spectrometry, which can damage the samples and affect subsequent measurements.

Where’s the heat?

As the Moon cooled off and volcanic activity slowed, elements that are incompatible with crystallization became concentrated in the remaining magma and eventually erupted as basalts that are enhanced in what’s known as KREEP: potassium, rare-earth elements, and phosphorus. Those basalts also are enriched in heat-producing elements, including radioactive uranium, thorium, and potassium.

Elardo says that thermal models of the basalts recovered by *Chang'e 5* can explain how they melted 2 billion years ago by top-down heating of shallow mantle rocks from a cover layer of KREEP basalts, which acted like an electric blanket.⁸ But even radioactive heat slows down with time. Because of uncertainties about the exact volume, placement, and concentrations of KREEP basalts on the Moon, it’s unclear whether they could provide enough heat to fuel volcanism within the last 120 million years. “I don’t think it’s necessarily something that we would expect,” says Elardo. “But what we expect is kind of meaningless. What nature makes is more important.”

More studies of young lunar volcanism are in the works. NASA has plans to take *in situ* age measurements of the largest irregular mare patch, Ina, as part of the Artemis program, possibly as soon as 2027. The planned instrument suite, Dating an Irregular Mare Patch with a Lunar Explorer (DIMPLE), will use a rover to collect samples and then laser-ablate them to collect rubidium–strontium age data.

Sarah Braden, a DIMPLE payload project scientist, says that the instrument should provide a clear constraint on whether Ina is 30 million years old, as her own crater counts have estimated,⁵ or billions of years old. The uncertainty of the rubidium–strontium ages will depend on how much of those elements are in the rocks. If they’re able to collect a measurement, even one on the high end of calculated uncertainty, says Braden, that big-picture question should be answered: “It’s a way to get answers to questions that would otherwise only be answerable in sample returns.”

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