## Uranium/lead dating provides most accurate date yet for Earth's largest extinction

By Robert Sanders

Image: A secondary electron microscopy image of a zircon from volcanic ash, about four thousandths of an inch (100 microns) across. The zircon has been cut and polished, then treated with high-temperature annealing and chemical abrasion with hydrofluoric acid. The crystal interior parts affected by lead loss have been "mined out" in the process, allowing uranium/lead dating to provide a more accurate measure of its age. (Image courtesy Josh Feinberg, UC Berkeley)

BERKELEY - A new study by geologists at the Berkeley Geochronology Center and the University of California, Berkeley, improves upon a widely used dating technique, opening the possibility of a vastly more accurate time scale for major geologic events in Earth's history.

In a paper published this week in Science, geochemist Roland Mundil of the Berkeley Geochronology Center (BGC) and his colleagues at BGC and UC Berkeley report that uranium/lead (U/Pb) dating can be extremely accurate - to within 250,000 years - but only if the zircons from volcanic ash used in the analysis are specially treated. To date, zircons - known to many as a semiprecious stone and December's birthstone - have often produced confusing and inaccurate results.
"Zircons have produced complicated data that are hard to interpret, though people have pulled dates out," said Mundil, a former UC Berkeley postdoctoral fellow now at the BGC, a non-profit scientific research institute dedicated to perfecting dating techniques for establishing the history of Earth and life on Earth. "Many of these studies will now have to be redone."

The U/Pb isotopic dating technique has been critical in dating geologic events more than 100 million years old, including volcanic eruptions, continental movements and mass extinctions.
"The beauty of this new technique is that we now can analyze samples we previously could not get an accurate date for," Mundil said. "This will have a big impact on radio-isotopic dating in general."

Mundil and his colleagues, including BGC director Paul Renne, adjunct professor of earth and planetary science at UC Berkeley, used this improved U/Pb technique to establish a more accurate date for the end of the Permian period
and the beginning of the Triassic period - 252.6 million years ago, plus or minus 200,000 years. This boundary coincides with the largest extinction of life on Earth, when most marine invertebrates died out, including the well-known flat, segmented trilobites.

Based on the improved U/Pb technique, the team also established that the argon/argon (Ar/Ar) isotopic dating technique that Renne employed for an earlier study of the Permian-Triassic boundary consistently gives younger dates, by about 1 percent. Renne ascribes this to a lack of a precise measurement of the decay constant of potassium. The technique is based on the fact that the naturally occurring isotope potassium-40 decays to argon-40 with a 1.25 billion year half-life. Comparison of the amount of argon-39 produced in a nuclear reactor to the amount of argon-40 gives a measure of the age of the rocks.

Uranium, on the other hand, is so well studied that its decay constant is much better known, making the U/Pb dating technique more accurate, Mundil noted. U/Pb dating relies upon the decay of naturally occurring uranium and different isotopes of lead.
"Further application of Mundil's approach will make the geologic time scale more accurate, letting us calibrate extinctions and important events in Earth's history, ranging from 100 million to several billion years ago, with unparalleled accuracy," Renne added.

The new U/Pb date, though about 2.5 million years older than Renne reported nine years ago based on Ar/Ar dating, nevertheless confirms his conclusion that the Permian extinction occurred at the same time as a major series of volcanic eruptions in Siberia. This is strong evidence that these eruptions caused, at least in part, the global die-off, which some scientists have ascribed to a meteor impact.

Mundil noted that in 1998, one group used U/Pb dating to assign a date of 251.4 million years ago for the main pulse of the Permina extinction, in apparent conflict with the new U/Pb age. That 'age,' however, "is based on interpretation of a very complicated data set," Mundil said.

Mundil and his colleagues set out to resolve the issue, using a new zircon pretreatment invented by UC Santa Barbara isotope geologist James M. Mattinson. The problem with using microscopic zircons, which are prevalent in volcanic ash, is that the decay of uranium to lead is so energetic that the lead atoms smash through and destroy the zircon crystal structure, which apparently allows some lead to leak out of the crystal, throwing off the analysis. Geologists have tried various zircon treatments, including abrading the outer surfaces of the crystals, which are typically a tenth of a millimeter across, or leaching the crystals with strong acid. Despite these treatments, the U/Pb method still produced a wide range of dates for zircons from the same layer of ash.

Mattinson's idea was to first heat or anneal the zircons, sealing off the least damaged areas of the crystal, then using a strong reagent, hydrofluoric acid, to eat away the heavily damaged areas.

When Mundil used this treatment, the zircon dates were much more consistent, requiring no selective interpretation of the data. The calculated uncertainty is about a quarter of a million years, which means the extinction took place over a very short time, the researchers concluded.

The zircons were obtained from ash layers located in central and southeastern China. The Meishan section in the latter region is accepted as the type locality for the Permian/Triassic boundary.

Whereas the U/Pb method yields ages which are more accurate, "Ar/Ar is still king in dating rocks younger than 100 million years and is about as precise as U/Pb methods, though we need to get better data for the decay constants to establish an absolute calibration," Renne said. "As soon as that calibration is put in place, the Ar/Ar method could become as accurate as U/Pb."

The work was supported by the National Science Foundation, the Australian Research Council and the Ann and Gordon Getty Foundation. Kenneth R. Ludwig of the BGC and Ian Metcalfe of the University of New England in Armidale, Australia, also participated in the study.

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## AGE OF THE EARTH

So far scientists have not found a way to determine the exact age of the Earth directly from Earth rocks because Earth's oldest rocks have been recycled and destroyed by the process of plate tectonics. If there are any of Earth's primordial rocks left in their original state, they have not yet been found. Nevertheless, scientists have been able to determine the probable age of the Solar System and to calculate an age for the Earth by assuming that the Earth and the rest of the solid bodies in the Solar System formed at the same time and are, therefore, of the same age.

The ages of Earth and Moon rocks and of meteorites are measured by the decay of longlived radioactive isotopes of elements that occur naturally in rocks and minerals and that decay with half lives of 700 million to more than 100 billion years to stable isotopes of other elements. These dating techniques, which are firmly grounded in physics and are known collectively as radiometric dating, are used to measure the last time that the rock
being dated was either melted or disturbed sufficiently to rehomogenize its radioactive elements.


Click on the image to see a graphical representation of geologic time

Ancient rocks exceeding 3.5 billion years in age are found on all of Earth's continents. The oldest rocks on Earth found so far are the Acasta Gneisses in northwestern Canada near Great Slave Lake ( $4.03 \mathrm{Ga} \mathrm{)} \mathrm{and} \mathrm{the} \mathrm{Isua} \mathrm{Supracrustal} \mathrm{rocks} \mathrm{in} \mathrm{West}$ Greenland ( 3.7 to 3.8 Ga ), but well-studied rocks nearly as old are also found in the Minnesota River Valley and northern Michigan (3.5-3.7 billion years), in Swaziland (3.4-3.5 billion years), and in Western Australia (3.4-3.6 billion years). [See Editor's Note.] These ancient rocks have been dated by a number of radiometric dating methods and the consistency of the results give scientists confidence that the ages are correct to within a few percent. An interesting feature of these ancient rocks is that they are not from any sort of "primordial crust" but are lava flows and sediments deposited in shallow water, an indication that Earth history began well before these rocks were deposited. In Western Australia, single zircon crystals found in younger sedimentary rocks have radiometric ages of as much as 4.3 billion years, making these tiny crystals the oldest materials to be found on Earth so far. The source rocks for these zircon crystals have not yet been found. The ages measured for Earth's oldest rocks and oldest crystals show that the Earth is at least 4.3 billion years in age but do not reveal the exact age of Earth's formation.

The best age for the Earth ( 4.54 Ga ) is based on old, presumed single-stage leads coupled with the Pb ratios in troilite from iron meteorites, specifically the Canyon Diablo meteorite. In addition, mineral grains (zircon) with U-Pb ages of 4.4 Ga have recently been reported from sedimentary rocks in west-central Australia.

The Moon is a more primitive planet than Earth because it has not been disturbed by plate tectonics; thus, some of its more ancient rocks are more plentiful. Only a small number of rocks were returned to Earth by the six Apollo and three Luna missions. These rocks vary greatly in age, a reflection of their different ages of formation and their subsequent histories. The oldest dated moon rocks, however, have ages between 4.4 and 4.5 billion years and provide a minimum age for the formation of our nearest planetary neighbor.

Thousands of meteorites, which are fragments of asteroids that fall to Earth, have been recovered. These primitive objects provide the best ages for the time of formation of the Solar System. There are more than 70 meteorites, of different types, whose ages have been measured using radiometric dating techniques. The results show that the meteorites, and therefore the Solar System, formed between 4.53 and 4.58 billion years ago. The best age for the Earth comes not from dating individual rocks but by considering the Earth and meteorites as part of the same evolving system in which the isotopic composition of lead, specifically the ratio of lead-207 to lead-206 changes over time owing to the decay of radioactive uranium-235 and uranium-238, respectively. Scientists have used this
approach to determine the time required for the isotopes in the Earth's oldest lead ores, of which there are only a few, to evolve from its primordial composition, as measured in uranium-free phases of iron meteorites, to its compositions at the time these lead ores separated from their mantle reservoirs. These calculations result in an age for the Earth and meteorites, and hence the Solar System, of 4.54 billion years with an uncertainty of less than 1 percent. To be precise, this age represents the last time that lead isotopes were homogeneous througout the inner Solar System and the time that lead and uranium was incorporated into the solid bodies of the Solar System.

The age of 4.54 billion years found for the Solar System and Earth is consistent with current calculations of 11 to 13 billion years for the age of the Milky Way Galaxy (based on the stage of evolution of globular cluster stars) and the age of 10 to 15 billion years for the age of the Universe (based on the recession of distant galaxies).

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