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U-Pb zircon age from the base of the Ediacaran Doushantuo Formation in the Yangtze Gorges, South China: constraint on the age of Marinoan glaciation

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The reported new U-Pb age by sensitive high-resolution ion microprobe (SHRIMP II) on zircon was obtained from a tuff sample at the basal Doushantuo Formation in the Jiuqudao section, which situated at the western limb of the Huangling anticline in the Yangtze Gorges in Zigui, Hubei, South China. Eighteen spots of zircons were analyzed and they form two clusters: one includes three spots, with an inherited age of 784 ± 15 Ma (MSWD=0.05); the other consists of 15 spots and gives a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 628.3 ± 5.8 Ma (MSWD=0.86). It is the first SHRIMP U-Pb zircon age obtained nearly the base of the Doushantuo Formation of Ediacaran and represents a maximum age of the Doushantuo Formation. It also forms an age constraint on the upper limit age of the Nantuo (Marinoan-type) glaciation.

Geological setting

The Doushantuo Formation of Ediacaran is located between the underlying Nantuo diamictite and the overlying Dengying dolostone in whole Yangtze platform, South China (Figure 1). However, the depositional age of the Doushantuo Formation has remained unsettled for a long time because no effective isotope dating method has been found for the carbonate-dominated sedimentary strata. Yang et al. (1994) reported an age of 645.4 ± 23.6 Ma in Sm-Nd

Figure 1 Geological sketch map of the studied area in Western Hubei, showing the distribution of the Ediacaran and Nanhua Systems and the sampling site (Jiuqudao section, black arrow). 1. Diorite, 2. Granite, 3. Ediacaran and Nanhua systems, 4. Cambrian System.

Figure 2 Photo showing the sampling site from the very thin bed of tuff in the basal Doushantuo Formation.

isochron from a phosphorite sample in the Doushantuo Formation. According to U-Pb age dates from Neoproterozoic sections in Siberia, Namibia and the Avalon Peninsula of Newfoundland, Knoll and Xiao (1999) suggested that the depositional age of the Doushantuo Formation is 550–600 Ma. Many researchers in several later articles agreed with this inference and furthermore determined the depositional age of the Doushantuo Formation to be ~570 Ma. Yin (2001) pointed out that the lower boundary age of the Doushantuo Formation should not be younger than 600 Ma, probably is between 600 and 650 Ma. Barfod et al. (2002) obtained a Lu-Hf age of 584 ± 26 Ma and a Pb-Pb age of 599.3 ± 4.2 Ma from the phosphatic deposit of the Doushantuo Formation at Weng'an area.

Petrological characteristics of the sample

The reported sample collected from the Jiuqudao section and the sampling site is about 2 m above the lower boundary of the Doushantuo Formation (latitude $30^{\circ}53'00''\text{N}$; longitude $110^{\circ}52'50''\text{E}$). The tuff is grayish green in the field and shows a grayish yellow color after weathered. It occurs as a very thin bed, only 1 to 1.5 cm thick (Figure 2). Zircons were separated according to magnetic properties and density and finally purified by hand and most of them are colorless or light yellow, transparent, euhedral equant or

Figure 3 Zircons from the base of the Doushantuo Formation.

prismatic in shape, and commonly have well-preserved crystal surfaces without any pronounced corrosion phenomenon. Cathodoluminescence images of zircons usually show distinct zoned structures and most of them range up to 100–150 μm in length (Figure 3).

U-Pb zircon geochronology

A total of 18 spots of zircons were analyzed and analytic results are shown in Figure 4. Most of them fall on the concordia and noticeably formed two clusters. One cluster consists of three spots with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 784 ± 15 Ma (MSWD=0.05). It was interpreted as an inherited age and represents the volcanic event in the early Nanhuan Period. The other cluster includes 15 spots and gives a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 628.3 ± 5.8 Ma (MSWD=0.86). This represents the age of the volcanic ash tuff of this horizon.

Discussion and conclusions

1. Study over the last two decades indicates that in the Doushantuo Stage of Ediacaran in South China, there are two fossil lagerstätten of the early Ediacaran. One is found from shale in the upper part of the Doushantuo Formation, which contains not only multicellular algae with complex bifurcated structures but also body compressions of metazoans. The other fossil lagerstätten was found in phosphatic and siliceous rocks in the lower to middle part of the Doushantuo Formation, which was represented by the microfossil assemblages found in phosphorites at the Weng'an area, Guizhou, and black chert nodules in the eastern Yangtze

Figure 4 U-Pb concordia diagram for T41017-3 from the Doushantuo Formation.

Gorges, Hubei. It contains not only large acanthomorphic acritarchs and well-preserved multicellular algal thalli with tissue differentiation and specialized reproductive organs, but also earlier metazoans and embryo fossils. As mentioned above, the age of 628.3 ± 5.8 Ma represents the age of the volcanic tuff at the base of the Doushantuo Formation. Therefore, it forms an age constraint on the maximum age of the fossil assemblage in the Doushantuo carbonate and phosphatic rocks, while the age of 599.3 ± 4.2 Ma (Barfod et al., 2002) is more likely to represent the age of the radiation period of the Weng'an biota. This age is very close to 630 Ma for the base of the Ediacaran System in the International Stratigraphic Chart (Gradstein et al., 2004) and is a very important age.

2. The sedimentary and chemostratigraphic data suggest that the Doushantuo cap dolostone is a Marinoan-type cap carbonate (Jiang et al., 2003), and additional radiometric ages recently obtained from South China allow a Marinoan age for the Nantuo diamictite (Zhou et al., 2004). During the last decade, published radiometric dates loosely constrain the age of the Marinoan-type glaciation as between 660 Ma and 600 Ma (Kendall et al., 2004; Calver et al., 2004; Zhou et al., 2004). A more robust constraint on the timing of Marinoan-type glaciation has been obtained from the Ghaub Formation in Namibia recently (Hoffmann et al., 2004). It is dating of 635.5 ± 1.2 Ma obtained on an ash bed interbedded with distal glaciomarine facies and provides a direct depositional age of the glaciogenic Ghaub Formation in Namibia. Our result is consistent with the 635 Ma age of the Ghaub glaciation and further constrains the upper limit age of the Marinoan-type glaciation and the maximum limit for the lower boundary of the Ediacaran System.

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Decay constants in geochronology

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Geologic time is fundamental to the Earth Sciences, and progress in many disciplines depends critically on our ability to measure time with increasing accuracy and precision. Isotopic geochronology makes use of the decay of radioactive nuclides as a help to quantify the histories of rock, minerals, and other materials. Both accuracy and precision of radioisotopic ages are, at present, limited by those of radioactive decay constants. Modern mass spectrometers can measure isotope ratios with a precision of 10^{-4} or better. On the other hand, the uncertainties associated with direct half-life determinations are, in most cases, still at the percent level. The present short note briefly summarizes progress and problems that have been encountered during the Working Group's activity.

The last major collective effort by the geological community to define a convention for decay constants is over a quarter of a century old; the IUGS recommendation in use today was published by Steiger & Jäger (1977). Subsequent research has introduced new radioisotopic geochronometers (e.g., Sm-Nd, Re-Os, Lu-Hf) not considered by Steiger & Jäger (1977). Moreover, the previous convention did not evaluate uncertainties in the constants, an omission that may have promoted false optimism as to the accuracy of the values.

All long-lived radioactive nuclides have a low desintegration rate and their half-lives are therefore *a priori* difficult to measure precisely. Three approaches have been used, individually or in combination.

1. Direct counting of alpha, beta or gamma activity. The empirical observation that this class of experiments gives the widest scatter may suggest that (since at most one among all discrepant values can be right) most experimenters have underestimated or neglected systematic bias factors (see e.g. Begemann et al., 2001, for a review of analytical difficulties).
2. Measuring the radiogenic daughter accumulated from a known amount of radioactive parent, also referred to as ingrowth experiments. While simple in principle, in practice the long accumulation times of several decades and the inevitably "old-fashioned" characterization of the starting material decades earlier have resulted in only a few experiments so far.
3. Comparing isotopic ages obtained by two different mineral chronometers and adjusting the decay constant of one system so as to force agreement with the other one, which is more accurately known. Because the decay constant of ^{238}U is the most accurately known of all nuclides used by geochronologists, this amounts to normalizing ages to the U-Pb system. While this is the preferred method in the geological literature, it must be stressed that there are inherent difficulties in ensuring that the two analyses actually both pertain to one and the same short-lived ("point-like") geological event and that no subsequent perturbation has occurred. It is also critical that the U-Pb age for comparison be statistically robust and not the product of discordia regression (e.g. Schmitz et al., 2003).

Comparisons are mostly made on sufficiently old samples that have accumulated enough radiogenic daughters to measure precisely, which increases the possibility that the geological history of the analysed rock might have included a chemical, thermal, mechanical, or other perturbation capable of fractionating, homogenizing or otherwise corrupting the minerals' chemical and isotope systematics. Furthermore, all dating methods require the (explicit or implicit)

determination of the initial isotopic composition. Isochron dating assumes that all cogenetic minerals incorporated the same initial isotopic composition; the accuracy of any age will only be as good as the petrological characterization of equilibrium parageneses. As discussed in detail by Begemann et al. (2001), ideas on a mineral's ideality are much more restrictive in the present age, in which microchemical analyses are routine, than they were a quarter of a century ago, and our perception of isotopic closure has been changed.

A note of caution to present and future readers is that, although the precision and accuracy of decay constants may be improved, the beneficial effects on the precision and accuracy of geochronological experiments will only be guaranteed if the choice of petrologically and mineralogically well-characterized and fully equilibrated parageneses will be pursued with the same rigor as that employed for the calibration of decay constants. Similarly, there is no model-independent way to ensure complete daughter retention, so that consistency checks by context-assessment and redundant sample choice remain of vital importance.

Uranium

The decay constants of ^{238}U and ^{235}U to ^{206}Pb and ^{207}Pb are $1.551 \times 10^{-10} \text{ a}^{-1}$ and $9.849 \times 10^{-10} \text{ a}^{-1}$, respectively (Jaffey et al., 1971), with 95% confidence level uncertainties of 0.11 and 0.18%, respectively. It must be noted that, due to the good but finite precision of these determinations, the concordia curve itself has a finite width and is not infinitely precise. Concordance of a mineral data point is thus also expressed in terms of a probability (Ludwig, 1998). It should be noted that many so-called U/Pb ages are actually determined as $^{207}\text{Pb}/^{206}\text{Pb}$ ages, in which case the mathematical interaction of the ^{238}U and ^{235}U decay constants produces much larger error contributions (Ludwig, 2000).

Potassium

The Steiger and Jäger (1977) constants for the branched decay of ^{40}K to ^{40}Ca and ^{40}Ar are $4.962 \times 10^{-10} \text{ a}^{-1}$ and $0.581 \times 10^{-10} \text{ a}^{-1}$, respectively, corresponding to a total ^{40}K decay constant of $5.543 \times 10^{-10} \text{ a}^{-1}$. The basis for these constants was reviewed in detail by Min et al. (2000), who concluded that the age uncertainty due to realistic error in these constants is at least 2% at the 95% confidence level. In $^{40}\text{Ar}/^{39}\text{Ar}$ dating, the problem is compounded by the use of a standard, whose age is also generally subject to decay constant errors. A solution involving comparison with U-Pb ages, which simultaneously gives both the total ^{40}K decay constant ($[5.476 \pm 0.034] \times 10^{-10} \text{ a}^{-1}$ at 95% confidence) and the age of the standard, was presented by Kwon et al. (2002). While application of this result does not require independent knowledge of the partial decay constants, these may be obtained by determination of the $^{40}\text{Ca}/^{40}\text{Ar}$ branching ratio in undisturbed old, K-rich materials (Nägler & Villa, 2000).

Rubidium

For the decay of ^{87}Rb to ^{87}Sr , the decay constant in widest use is $1.42 \times 10^{-11} \text{ a}^{-1}$, with an uncertainty of 1% (Steiger and Jäger, 1977). As reviewed in detail by Begemann et al. (2001), two factors may have biased the results. Firstly, the ingrowth experiments

(Davis et al., 1977) obtained a range of values rather than a single one because the initial isotopic composition of the Sr which would have to have been known in 1956 had not been measured with sufficiently accurate and precise protocols. Secondly, the IUGS committee considered comparisons with K-Ar ages on non-stoichiometric micas, now thought to have been altered and/or unlikely to record the exact same point in time for the two systems. A newer estimate of $(1.402 \pm 0.008) \times 10^{-11} \text{ a}^{-1}$ based on comparing whole-rock Rb-Sr and Pb-Pb data from meteorites (Minster et al., 1982) differs by ca. 1% from the Steiger & Jäger (1977) value, and is currently used by some meteorite researchers. A value of $(1.396 \pm 0.009) \times 10^{-11} \text{ a}^{-1}$ is supported by new β^- counting data (Kossert, 2003).

Samarium

The ^{147}Sm - ^{143}Nd dating method has come of age after the IUGS convention (e.g. Lugmair and Marti, 1978). Measuring the alpha decay constant is not excessively difficult and the value of $6.54 \times 10^{-12} \text{ a}^{-1}$ is adopted without controversy by all practitioners in the field. The error obtained by pooling the more recent and precise alpha-counting data is of order 1%.

Lutetium

The ^{176}Lu - ^{176}Hf dating method also came into widespread use after 1977, and uncertainty about the decay constant has recently received much attention. ^{176}Lu is a beta emitter and counting experiments have accordingly yielded vastly conflicting results (Begemann et al., 2001). Geological intercomparisons with U-Pb or Pb-Pb have not fully clarified the issue. Of special concern is the report by Scherer et al. (2003) which presents data from one and the same laboratory (thereby eliminating the possibility of interlaboratory bias, which is not unrealistic for a chemically very delicate element pair such as Lu and Hf). These authors calculate a decay constant of $(1.96 \pm 0.04) \times 10^{-11} \text{ a}^{-1}$ from meteorites but one of $(1.869 \pm 0.016) \times 10^{-11} \text{ a}^{-1}$ from terrestrial rocks, well outside the estimated 95% confidence level uncertainties. As clearly both cannot be simultaneously correct, we must conclude that a heretofore unrecognized violation of the "point-like event" condition is affecting at least one of the two data-sets. While terrestrial data were obtained on internal isochrons based on mineral analyses from equilibrium magmatic parageneses, the meteorite data represent whole-rock analyses. In agreement with the general requirements laid out in the introduction, the latter may be suspected of hiding initial isotopic heterogeneities unless proved to be cogenetic by non-isotopic means. An alternative hypothesis, that ^{176}Lu has a significant electron capture decay branch, has been recently ruled out by two independent methods (Amelin et al., 2003; Norman et al., 2003).

Rhenium

The decay constant of ^{187}Re to ^{187}Os presently in use is $1.666 \times 10^{-11} \text{ a}^{-1}$ (Smoliar et al., 1996), on the basis of geological intercomparisons and ingrowth experiments. These authors estimate an uncertainty of 1% for their proposed value.

Platinum

The most recent assessment of the ^{190}Pt - ^{186}Os decay constant is $1.477 \times 10^{-12} \text{ a}^{-1}$ (Walker et al., 1997) on the basis of geological comparisons and ingrowth experiments, and taking into account a new determination of the Pt isotopic composition. These authors estimate an uncertainty of 1% for their proposed value.

Units

Because some confusion has arisen in recent years, it is useful to reiterate correct usage of units. The SI unit of time, the second (s), is fairly impractical for geologists and for nuclear physicists alike; in such cases the SI system tolerates other units. The unit of time for geological applications is the annum (a), where $1 \text{ a} = 3.16 \times 10^7 \text{ s}$ (Holden, 2001).

Following correct SI usage (Nelson, 2002), units obey algebraic rules (e.g. $5\text{a} - 3\text{a} = 2\text{a}$; $1 / (2\text{a}) = 0.5 \text{ a}^{-1}$) and therefore one and the same unit must be consistently used in absolute and relative measurements. Ages and time intervals must be expressed in a (ka, Ma, Ga); velocities, rates, and decay constants must be expressed in a^{-1} (ka^{-1} , Ma^{-1} , Ga^{-1}) (Holden, 2001) and should never be mixed up with other units as is commonly done in using e.g. Ma for absolute age, but m.y. for age differences. The consistent use of only one unit for time is analogous to, e.g., the use of only one unit for temperature: temperature differences and gradients are correctly expressed by an intrinsically absolute unit such as the °C. Similarly, the meter (m) is used to indicate both an absolute depth and a depth difference.

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