Early Cambrian ocean anoxia in South China

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The cause of the most marked changes in the evolution of life, which define the first-order stratigraphic boundary between the Precambrian and the Phanerozoic eon, remains enigmatic and a highly topical subject of debate. A global ocean anoxic event, triggered by large-scale hydrogen sulphide (H_2S) release to surface waters, has been suggested by Wille *et al.*[1], on the basis of two data sets from South China and Oman, to explain the fundamental biological changes across the Precambrian/Cambrian (PC/C) boundary. Here we report a new precise SHRIMP U–Pb zircon age of 532.3 ± 0.7 million years (Myr) ago (Fig. 1) for a volcanic ash bed in the critical unit that reflects the ocean anoxic event, the lowermost black shale sequence of the Niutitang Formation in the Guizhou Province, South China. This age is significantly younger than the precise PC/C boundary age of 542.0 ± 0.3 Myr ago[2], approximately 10 Myr younger than the extinction of the Ediacaran fauna, and thus challenging the view of a major ocean anoxic event having been responsible for the major changes in the direction of evolution at the PC/C boundary.

So far no reliable precise radiometric data have been available to constrain the age of the widespread Lower Cambrian black shale series (extending over some 1,600 km in a northeasterly direction along the Yangtze Platform) above the PC/C boundary in South China. Wille *et al.*[1] used an imprecise Re–Os age (541 ± 16 Myr ago) of a distinct Ni–Mo sulphide marker bed in the lowermost part of the Niutitang Formation black shale sequence as a basis for their suggestion that a global "sulphide poisoning" caused the drastic changes of life and its distribution across the PC/C boundary. Our new precise SHRIMP U–Pb zircon age data (Fig. 1) from a volcanic ash bed just below the Ni–Mo sulphide marker in the lowermost Niutitang Formation now suggests that the Ni–Mo sulphide precipitation cannot have occurred before 532.3 ± 0.7 Myr ago. By then, the first stage of the 'Cambrian explosion'—documented by the rapidly expanding trace and body fossil record and a greatly diversifying multiphyletic small shelly fauna (summarized by ref. 3)—was well underway.

A global transient signal was proposed by Wille *et al.*[1] by jointly plotting Mo isotope data from the Ni–Mo sulphide bed, positioned several metres above the PC/C boundary, with data from shale samples collected from other localities in South China (Ganziping and Yuanling) and in Oman, assuming that all of these samples are contemporaneous (Fig. 1 of ref. 1). Our new age data show that this assumption is not justified because stratigraphic thickness above the PC/C boundary marker does not translate linearly into a single timescale for these locations. The sections studied in South China include a prolonged disconformity, overlain by a diachronous transgression of the basal Niutitang and Zhujiajing Formations (Guizhou and Yunnan Provinces, respectively). At the PC/C section studied by us in the Guizhou Province, most of the 10-Myr time span between the top of the Precambrian Dengying Formation and the dated volcanic ash bed appears to be represented by a hiatus at the lithostratigraphic boundary. The new age data therefore offer a reliable constraint on the maximum duration of non-sedimentation at the PC/C boundary (that is, approximately 10 Myr), which is widespread on the Yangtze Platform[4].

Although upwelling of H_2S-rich deep ocean water may still be a good explanation for the widespread black shale deposits and their unusual metal contents, a sea-floor hydrothermal venting event also remains a viable alternative in the Chinese sections[5–7]. In conclusion, the new age data show that the assumption made by Wille *et al.*[1] that the Mo isotope signals in the sections from Oman and South China are contemporaneous cannot be upheld, hence their global significance must be questioned.

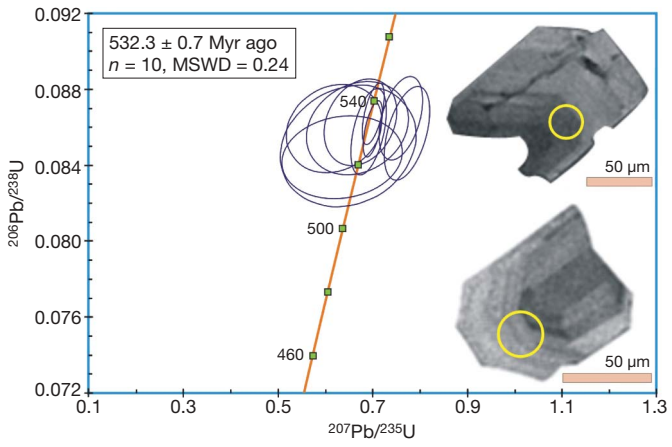

Figure 1 | U–Pb concordia plot for zircon grains from a volcanic ash bed in the lowermost black shale sequence of the Niutitang Formation in Guizhou Province, South China. The analysed spots shown in yellow circles and the zircons display a clear oscillatory magmatic zonation (see inserted cathodoluminescence images) without inherited cores and were therefore chosen for constraining the age of crystallization (that is, 532.3 ± 0.7 Myr ago; with 1 SE error and MSWD (mean square of weighted deviates) = 0.24).

METHODS

Sample ZN0909 was collected in 2007 from a volcanic ash bed in a road-cut approximately 200 m east of the Zhongnancun section (27° 41′ 24.6′′ N, 106° 40′ 45.2′′ E). Zircons were extracted from approximately 10 kg of rock sample, mounted, polished and examined. The prismatic grains range in length from 70 to 150 µm. Most of them are euhedral, colourless, transparent and cracked to various degrees. We measured absolute abundances of U and Pb and their isotopic ratios of zircons on the SHRIMP II ion microprobe at Curtin University, Perth, through the Remote Operation System at the Beijing SHRIMP Center.

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Jiang *et al.*[1] present a new SHRIMP U–Pb zircon age of 532.3 ± 0.7 million years (Myr) ago for an ash bed in the lowermost black shale sequence of the Niutitang Formation, China, and claim that the data presented in our recent paper[2] do not firmly support the idea that the biological and environmental changes at the Precambrian/Cambrian transition can be explained by a single global hydrogen sulphide (H_2S) release event. Their new age seems to be supported by another recent SHRIMP investigation[3] which indeed suggests that the Chinese metal-enriched sulphide layer does not represent the Precambrian/Cambrian boundary and shows that the redox history of both basins (Oman and South China) was much more complex.

However, as outlined previously[4], SHRIMP data are not always reliable when it comes to solving stratigraphical problems. For example, with regards to the Yangtze platform, SHRIMP data on the lowermost Doushantuo Formation gave an age of 621 ± 7 Myr ago[5], whereas single zircon U–Pb data gave an age of 632.5 ± 0.5 Myr ago[6]. This offset is very similar in value and direction to the offset between the Precambrian/Cambrian boundary and the SHRIMP age of Jiang *et al.*[1]. If indeed this is related to a systematic inaccuracy of the applied SHRIMP technique, it seems inevitable that single zircon analyses must be undertaken to solve the age problem in the case under discussion.

New age data[7] confirm an age of 542–541 Myr ago for the base of the Ara A4 cycle, and point to a stratigraphic time interval for the measured section of ~1 Myr. This is in good agreement with the time generated by our model, in favour of an ocean overturn in the lowermost Cambrian. If the age of 532.3 ± 0.7 Myr ago in China can be confirmed, the Mo isotopic signals from Oman and South China would be of diachronous origin. They would thus reflect two successive events, each one less resolved than the initially suggested combined profile. This would affect the temporal resolution and render the quantifications of the model of ref. 2 more uncertain, but would not affect the model's main qualitative conclusion. The most plausible explanation for the Mo isotopic excursions observed in both basins in combination with the same overall Mo isotopic composition is a transient Mo seawater signal caused by excess H_2S.

Jiang *et al.*[1] seem to suggest that the unusual metal enrichment in the Chinese black shales may not be related to scavenging from sea water in a euxinic environment, but from sea-floor hydrothermal venting. However, our Mo isotope data exclude a hydrothermal origin of molybdenum, which is the element most enriched in these rocks, together with a broad suite of other redox-dependent metals[8]. The consistent $\delta^{98/95}$Mo value of 1.1 ± 0.1‰ in the basal sulphide marker bed defines the Mo isotope composition of the sea water at that stratigraphic time interval, and the subsequent oscillation of Mo isotope composition in the overlying shale attests to a transitional seawater signal. It remains to be tested in other stratigraphic sections if this oscillation is indeed a global signal, possibly over an extended 10-Myr time interval in the Early Cambrian.

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