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An Extraterrestrial Impact at the Permian-Triassic Boundary?

Becker *et al.* (1) presented geochemical evidence that suggests that the largest mass extinction in Earth history, at the Permian-Triassic boundary (PTB) 250 million years ago (Ma), coincided with an extraterrestrial impact comparable in size to the one that likely caused the end-Cretaceous extinctions 65 Ma (2). Although Becker *et al.* analyzed material from sections in Hungary, Japan, and China, the Hungarian section yielded no extraterrestrial signature, and their identification of the PTB in the Japanese section is questioned in the accompanying comment by Isozaki (below). Thus, only their analyses of the Chinese section provide hitherto uncontested evidence for an impact at the boundary—in the form of data on the abundance and composition of fullerenes in the “boundary clay,” a volcanic ash layer called Bed 25 at Meishan, China (3). Although fullerenes may be purely terrestrial [see, e.g., (4)], Becker *et al.* report that the fullerenes from the Meishan ash carry extraterrestrial noble gases in the cage structure, rich in ^3He and with distinctive $^3\text{He}/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, and that this signature therefore derived from a bolide impact. Here, we report that we are able to detect fullerene-hosted extraterrestrial ^3He neither in aliquots of the same Meishan material analyzed by Becker *et al.*, nor any in samples of a second Chinese PTB section, and that we thus find no evidence for an impact.

Becker *et al.* reported helium in bulk rock

and in fullerenes extracted from Meishan Bed 25 following acid demineralization. Their two aliquots of bulk rock yielded 0.43 and 0.58 pcc/g (10^{-12} cc g^{-1} at standard temperature and pressure) of ^3He . From 40 g of rock, Becker *et al.* extracted 14 μg of fullerene that yielded very high ^3He concentrations, implying that fullerene-hosted helium accounted for at least 0.052 pcc/g of the ^3He in Bed 25; this number could be higher, because Becker *et al.* provided no indication of fullerene extraction efficiency.

We first analyzed 15 aliquots of bulk rock from Bed 25, provided by S. Bowring to be representative of the material he supplied to Becker *et al.* Samples were initially dried in an oven for 2 hours at ~ 90 to 100°C to drive off adsorbed water. Based on stepped-heating results on fullerenes (1), no ^3He would have been lost during sample drying. We then gently powdered 150 g of rock by hand with a mortar and pestle and thoroughly homogenized the sample. Ten aliquots (~ 350 mg each) were drawn from this homogenized powder; the remaining five aliquots were taken from several different clumps of the material to assess spatial heterogeneity. Samples were fused under vacuum at 1400°C following procedures reported earlier (5), except that the acetic acid step, designed to remove CaCO_3 , was not used on these carbonate-poor rocks. None of these samples yielded a significant amount of ^3He (Fig. 1): The

mean of the 15 runs was 0.005 pcc/g, and the maximum for any single aliquot was only 0.01 pcc/g. We obtained similar results from six samples of the stratigraphically equivalent bed at Shangsi, China (also provided by Bowring). Hence, we obtained ^3He concentrations from bulk rock samples that were a factor of 45 to 150 lower than those reported by Becker *et al.* To ensure that we were quantitatively extracting all the He at 1400°C , we outgassed a single sample at 1800°C after fusion at 1400°C ; no additional ^3He was released.

We then demineralized a 16 g aliquot of Meishan Bed 25, following the same HF- BF_3 digestion procedure (6) used by Becker *et al.* This residue contained only 0.003 pcc of ^3He per gram of starting material. Because the demineralized residue does not contain significant ^3He , fullerene-hosted ^3He within this residue cannot be significant either, so we did not isolate fullerene for noble gas analysis. This experiment places an upper limit on the fullerene-hosted ^3He in Bed 25 that is a factor of 15 lower than the concentration reported by Becker *et al.* (1).

The helium we obtained from Bed 25 samples is reasonable for a 250-million-year-old volcanic ash bed. Large inter-aliquot variability in ^4He content and the survival of most ^4He through HF demineralization (Fig. 1) suggest that accessory zircons, known to exist in Bed 25 (3), control the distribution of this isotope. The ^3He concentration and $^3\text{He}/^4\text{He}$ ratio (average $<0.003 R_A$) of Bed 25 are lower than we obtained from several hundred deep-sea carbonate sediments [see, e.g., (5)] and are at the low end of the range expected for purely terrestrial radioactive decay processes (7). The dearth of ^3He from interplanetary dust particles (IDPs)—not to be confused with a fullerene-hosted impact signature—is not surprising, because Bed 25 is a volcanic ash and was likely deposited quickly.

We thus find no evidence for the impact-derived ^3He reported by Becker *et al.* Our analytical technique for ^3He is as sensitive and precise [see details in (5)] as that used by Becker *et al.*, so the discrepancy between our results and theirs is probably not analytical in origin. Sample heterogeneity is also an unlikely explanation: Although Becker *et al.* found substantial ^3He in all three aliquots they analyzed (a total of 41 g of rock), we were unsuccessful in detecting extraterrestrial ^3He in any of our 22 aliquots (150 g of homogenized Bed 25 in 10 aliquots, 1.5 g of spatially distributed spot samples in five aliquots, and 16 g of demineralized rock in one aliquot from Meishan, as well as 2 g of rock in six aliquots from three samples of the Shangsi P-Tr boundary bed).

Without confirmation of fullerene-host-

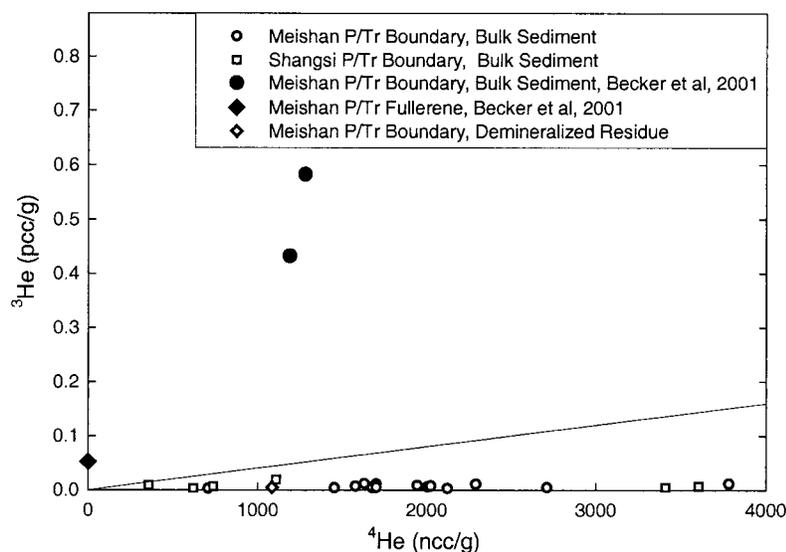


Fig. 1. He isotope data for Chinese PTB samples. Filled symbols, Becker *et al.* (1); open symbols, this study.

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ed ^3He in Bed 25, both the occurrence of an extraterrestrial impact and the cause of the mass extinction at the PTB must remain open questions.

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Becker *et al.* (1) reported an anomaly in ^3He trapped in fullerene from PTB rocks from Japan and China, which in turn suggested a possible extraterrestrial impact as the cause of the PTB mass extinction. Although the approach of using the ^3He signature appears promising, the stratigraphy of the Sasayama section in Japan poses a major problem that is fatal to their conclusion: The PTB horizon is missing in this section, and the " ^3He -enriched" sample they analyzed has actually come from at least 0.8 m (and possibly much further) below the PTB.

Owing to absence of good index fossils, the Sasayama section is dated by correlation with other sections. The PTB sections of deep-sea chert facies have been examined in more than ten sections in Japan (2, 3); all showed a constant lithostratigraphy that comprised, from bottom to top, (i) Late Permian bedded chert, (ii) latest Permian siliceous claystone or shale, (iii) boundary black organic claystone, (iv) Early Triassic siliceous claystone, and (v) late Early to Middle Triassic bedded chert. The lower chert and siliceous claystone are characterized by Chanhsingian (late Late Permian) radiolarians such as *Neoalibaillella optima* and *Alibaillella triangularis* (4), and the upper siliceous claystone and chert contain distinct Early Triassic forms. The central black claystone, less than 5 m thick, yields only ill-preserved microfossils and thus is not dated precisely. Nevertheless, these data indicate that the PTB horizon is somewhere within the black claystone (2), not in the lower siliceous claystone. Thus the " ^3He -enriched" sample of Becker *et al.* (1) was clearly collected from the Late Permian interval at least 0.8 m below the PTB.

Making the situation worse, this section is cut in the middle by a fault, with gouge and chert breccia [described as sheared black shale in figure 2 of (1)] that has removed beds nearly 20 to 30 m thick between the lower siliceous claystone and the upper chert. Thus, not only does the section lack the PTB horizon, but this faulting has removed an additional, undetermined interval of time between the claimed " ^3He -enriched" sample and the PTB. In any case, the Permian radiolarians and conodonts survived even above this " ^3He -enriched" horizon up to the top of the siliceous claystone. This suggests that the alleged impact event did not terminate such cosmopolitan marine biota that flourished throughout the Permian and finally disappeared at PTB.

At least for confirming the background absence of ^3He in adjacent horizons immediately above and below PTB, Becker *et al.* should have checked better PTB sections and used more samples collected following a double-blind protocol. Becker *et al.* also reported a similar ^3He spike from Bed 25 (a volcanic tuff of terrestrial origin) immediately below PTB in the Meishan section in China. Because the " ^3He -enriched" sample from Sasayama is significantly older than Meishan Bed 25, they cannot have been from the same impact event.

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Response: In our study (1), we suggested that an impact event occurred at the 250-million-year-old PTB, triggering the most severe mass extinction in the history of life on Earth. By exploiting the unique ability of the fullerene molecule to trap noble gases inside of its caged structure, we were able to determine whether the origin of the fullerenes was extraterrestrial (ET) or terrestrial. We have found fullerenes with ET helium associated with extinction events in five locations at the 65-million-year-old Cretaceous-Tertiary boundary (KTB) and in two locations at the PTB (1, 2). Although it has been suggested that the fullerenes isolated from some KTB sediments may have been associated with terrestrial causes—specifically, with global wildfires triggered by the impact event—it has now been accepted that the KTB fullerenes are extraterrestrial, deliv-

ered exogenously to the Earth during the impact itself (3, 4).

Farley and Mukhopadhyay, at Caltech, report that they have measured background levels of ^3He across the PTB in sections in Meishan and Shangsi, China, and have concluded that there is no evidence for the delivery of ET material to the Earth by a bolide. Rather, their results are consistent with helium present in a 250-million-year-old ash layer found at both boundary sections. We observed significant differences between the procedures we used and those carried out during their study, however, and we believe that these differences influenced the outcome of their experiments.

In our study, we obtained a ~ 75 -g sample of Bed 25 from S. Bowring that contained the base of this unit, which represents the time interval during which more than 90% of all marine organisms, most of the terrestrial vertebrates, and many plants were brought to an abrupt extinction (1, 5, 6). Because we were interested in focusing on this discrete event rather than looking at the continuous flux of ^3He throughout Bed 25, we separated out the carbon-rich basal material, characterized by an interstratified reddish-gray montmorillonite-illite clay layer. This reduced our bulk sample to the ~ 40 g of material that was demineralized using the procedures outlined in (1). The acid residue (442 mg) that represented about 1% of the original material was extracted with solvents to isolate the fullerene component (14 μg). In contrast, the Bed 25 ash, provided to us by the Caltech group, contained less than 0.1% (or 6 mg in 7 g of ash) acid-resistant residue, and that fraction appeared to be mostly resistant silicates such as zircon. Thus, our contention is that the Caltech sample contained neither the organic carbon carrier for the ^3He -rich fullerene component nor the carrier (whatever it may be) for the bulk ^3He or background flux. Our bulk ^3He concentrations in two aliquots of the PTB sample yielded values of 0.43 and 0.58 pcc/g, while several samples above and below the boundary had ^3He concentrations about 10 times lower (≤ 0.02 to 0.2 pcc/g) (7).

To further assess the variability in bulk ^3He measured for the Meishan samples collected at the boundary (Bed 25) and in samples directly above and below this interval, we also obtained a separate suite of Meishan samples from S. D'Hondt. The samples collected by D'Hondt were evaluated for $\delta^{13}\text{C}$ and compared to replicate samples measured in (5). This material also represented the changes in lithology at the base of Bed 25 and in the sediments above and below. These samples had even more ^4He (3 to 10 $\mu\text{cc/g}$) than the samples measured in either our study (1) or that of Farley and Mukhopadhyay. In our case, the high ^4He concentrations made it

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impossible to evaluate the ^3He concentrations because the $^3\text{He}/^4\text{He}$ ratio was at the abundance sensitivity limit. Unfortunately, our samples were not available for reassessment of the bulk ^3He upon submission of the comment by Farley and Mukhopadhyay. We have since reproduced our own results with four replicate analyses of the boundary layer. The ^3He concentrations at the Meishan boundary range from 0.15 to 0.5 pcc/g. We will also provide our samples to two separate labs for independent measurements of the bulk ^3He . We are confident that these labs will reproduce our results (1) and will further demonstrate the differences in the samples provided by S. Bowring to Caltech and us.

The differences in bulk ^3He and ^3He fullerene concentrations appear to be directly attributable to sample selection and preparation. By homogenizing a 150-g sample of volcanic ash, Farley and Mukhopadhyay may reduce the variability and noise in the ^3He signature, an important consideration when examining long-term IDP flux signals. We concur with their conclusion that the volcanic ash would have been deposited very rapidly and would not preserve the extraterrestrial signature attributed to IDPs. However, when examining "event markers" such as fallout from a bolide impact, the homogenization strategy would severely dilute the already weak ^3He signal present in the bulk ash. Variations in the carbon content and ^3He concentrations in the Bed 25 samples clearly point to the fact that the two groups examined very different samples. The change in lithology at the base of Bed 25 apparently makes a significant difference in the identification of the bolide event marker, and care must be taken to identify and quantify the helium carriers present in the boundary.

In a separate comment, Isozaki suggests that the fullerenes we detected in the siliceous claystone at Sasayama did not come from the PTB. Instead, using lithostratigraphy, he places the true boundary somewhere within the carbonaceous claystone above this interval. However, as pointed out both by Kakuwa (8) and in Isozaki's comment, the PTB cannot be precisely defined in any of the Japa-

nese sections because of poor stratigraphic control. Moreover, neither the siliceous claystone nor the carbonaceous claystone have age-diagnostic fossils to properly date the boundary at Sasayama or in any of the Japanese sections (8), as the comment by Isozaki acknowledges.

The principal difference underlying our placement of the boundary compared with that of Isozaki rests on the mechanism that led to the PTB mass extinction. Isozaki favors a model involving overturn of CO_2 -saturated deep anoxic water, coupled with a hypothesized "hypercapnia" that apparently lasted some 20 million years (9). As pointed out by Gin *et al.* (5), however, the mass extinction that occurred at the PTB was abrupt, lasting only a few 100,000 years. Our boundary sample, provided by M. Rampino, was selected based upon evidence for an extraterrestrial cause (10, 11). So far, we have only found fullerene at the boundary, and not in significant concentrations above and below (1, 2). Thus, in the absence of any biostratigraphy and poor stratigraphic control (8), we feel that the best interpretation for the boundary at Sasayama is in the siliceous claystone, where fullerene and other extraterrestrial signatures have been identified (1, 10, 11).

Perhaps the most significant drawback to our investigation of the PTB to date is the lack of geographic spread and the inability to demonstrate that other extraterrestrial signatures, like those reported in some KTB sites (1), are also present in the PTB. New results on sediments collected from the Meishan PTB show that Fe-Si-Ni grains are concentrated in the top 2 cm of Bed 24e and in the overlying basal portion of Bed 25 (12). These Fe-Si-Ni grains are produced at very high temperatures (Fe, 2890°C; Ni, 2863°C; Si, 2227 °C), and are thus inconsistent with a volcanic origin but consistent with impact-metamorphosed grains found in some impact craters and in sediments associated with the KTB (12, 13). Interestingly, some Fe-rich nuggets have also been reported in the siliceous claystone at Sasayama (14). Based on these new results, it would appear that an impact

event of global proportions remains the best explanation for the most severe biotic crisis in the history of life on Earth.

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7. These values should have been reported as upper-limit concentrations in our paper (1), because the VG5400 mass spectrometer has an abundance sensitivity of 10^8 for helium. A significant fraction of the ^3He signal for nonboundary samples at Meishan is from the low-energy tail of the ^4He (the MAP 215–50 mass spectrometer used by Caltech does not have this limitation).
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