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Absence of extraterrestrial ^{3}He in Permian–Triassic age sedimentary rocks

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Abstract

Helium concentration and isotopic composition were measured in a suite of samples across the Permian–Triassic boundary at Opal Creek, Canada, to determine whether high extraterrestrial helium concentrations are associated with a possible extinction-inducing impact event at this time. No extraterrestrial ^{3}He was detected, implying that neither fullerene-hosted nor IDP-hosted He is present at or near the boundary. This observation is consistent with similar studies of some Permian–Triassic sections, but contrasts sharply with reports of both fullerene- and IDP-hosted extraterrestrial ^{3}He at other sections.

Step-heat experiments indicate rapid diffusion of extraterrestrial helium from sediments heated to temperatures above ~70 °C. Given the likelihood of burial and associated heating in Permian–Triassic age rocks, the initially unexpected absence of IDP-hosted ^{3}He likely indicates thermally induced diffusive loss. Indeed one of the key sections (Graphite Peak, Antarctica) from which extraterrestrial ^{3}He has been reported at and near the Permian–Triassic boundary has been sufficiently heated that the reported preservation of extraterrestrial helium, in both IDPs and fullerenes, is inexplicable. Recent contamination provides a plausible explanation for extraterrestrial ^{3}He in these samples.

While no extraterrestrial ^{3}He was detected at Opal Creek, there is a sharp increase in nucleogenic ^{3}He very close to or at the Permian–Triassic boundary. This presumably arises from the major lithologic change at this time, from cherts in the Permian to shales and siltstones in the Triassic. Increased nucleogenic ^{3}He is associated with increases in both lithium and organic carbon content into the Triassic. Either the production rate or the retention of this ^{3}He is higher in the shales and siltstones than in the cherts. Care must be taken to eliminate such artifacts before interpreting changes in ^{3}He concentration in terms of fluctuations in the delivery of ^{3}He from space.

Keywords: extraterrestrial helium; cosmic dust; Permian-Triassic boundary; fullerene

1. Introduction

Multiple lines of evidence have been presented in favor of an extraterrestrial impact associated with the Permian–Triassic (PT) mass extinction. In the 1990s, a small Ir anomaly and microspherules [1], and shocked quartz [2] were described at the PT boundary. More recently PT age sediments were reported to carry extraterrestrial noble gases in fullerenes and IDPs [3,4] as well as unaltered meteorite fragments [5]. In addition a possible impact crater in the Indian Ocean has been

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alleged to be of the appropriate age [6]. These observations have been very controversial. Some of the original observations were not confirmed in the same or in other PT sections [7,8], the identification of the PT boundary in relation to the fullerene spike is doubtful in at least one case [9], and the existence of the Indian Ocean impact crater and its reported PT age have been rejected [10–12]. Although a great deal of very suggestive data has been published on the topic, no incontrovertible evidence for a PT-age impact yet exists.

The presence of high concentrations of extraterrestrial ^{3}He in sediments coincident (or nearly so) with the PT boundary would support the proposed impact event. ^{3}He might be present trapped within fullerenes released directly from the impactor [3] or in interplanetary dust particles (IDPs) [4]. While IDPs accumulate from multiple sources and need not be indicative of a significant extraterrestrial event, an enhanced IDP flux may be associated with showers of long period comets [13] and with major collisions in the asteroid belt [14]. Both of these events raise the likelihood of a terrestrial impact, in some cases enormously so [15]. Thus elevated IDP-hosted ^{3}He coincident with the PT boundary would provide indirect support for the occurrence of an impact. One advantage of using ^{3}He as an impact tracer is that elevated levels associated with major solar system events can last for a few million years [13,14], making detection far easier than locating a single ejecta layer in a long stratigraphic sequence.

Here we present results of He isotopic analyses across a well-studied PT boundary section to assess the presence of fullerene- or IDP-hosted ^{3}He. This work complements similar studies at Meishan and Shangsi, China [8], and in the Austrian Alps [16].

2. Setting, samples, and methods

Helium isotopes were measured in sedimentary rocks from the Opal Creek PT section in western Canada described by Henderson [17]. This site records a deep-water outer shelf environment composed of cherts in the Upper Permian Ranger Canyon unit and shales and siltsones in the uppermost Permian and lowermost Triassic Sulphur Mountain formation. The PT boundary has been identified based on conodont stratigraphy; it is characterized by black pyrite-bearing shales that likely indicate deposition in an anoxic environment. The average sedimentation rate through the sampled interval is about 2 cm/kyr. Thirty-three samples ranging from ~5 m below the PT boundary to ~40 m above the boundary were analyzed for helium, representing about 2.5 Myr. The densest sampling (few cm spacing) was undertaken near the PT boundary, while sampling away from the boundary was at several meter spacing.

Initially the ~1/2 g samples were decarbonated with acetic acid and the residue centrifuged prior to analysis [18]. As shown in Table 1, these samples contained very little acetic acid-soluble material (~20%), so for the remaining samples this step was omitted. Two samples were subjected for 12 h to hot concentrated 2:1 HF–HCl and then dried to isolate helium in acid-insoluble residue prior to analysis. These samples were then fused in vacuum at 1300 °C to release helium. For one additional sample He was extracted by incremental step heating of 1 h duration per step using a resistance furnace. Temperature uncertainties on this experiment are estimated to be ±30 °C.

Table 1
Helium in Opal Creek samples

Sample	Position (cm)	^{3}He (fmol/g)	^{4}He (pmol/g)	^{3}He/^{4}He ($\times 10^8$)	Non-carbonate fraction
224	3915	0.00242	138.8	1.82	Whole rock (WR)
216	3115	0.01339	185.3	7.28	WR
192	1810	0.00797	138.7	5.74	WR
177	1003.5	0.01495	477.4	3.22	WR
176	983.5	0.01042	235.4	4.48	WR
173	850.5	0.00869	337.1	2.52	WR
166	423.5	0.01082	370.3	2.94	WR
161	310.5	0.01053	288.2	3.64	WR
121	175.5	0.00820	332.9	2.52	WR
44	116.75	0.01324	402.6	3.36	WR
62	90.5	0.00983	474.4	2.10	WR
7	49.5	0.00286	316.2	0.98	0.81
8	48.5	0.00302	226.4	1.40	0.82
9	47.5	0.00292	325.7	0.98	0.82
10	46	0.00358	486.6	0.70	0.86
11	44.5	0.00345	298.3	1.12	0.82
12	43	0.00351	341.8	0.98	0.84
13	40	0.00305	302.8	0.98	0.83
13	40	0.00911	401.8	2.24	WR
14	37.5	0.00838	370.9	2.24	0.83
15	36.5	0.00297	241.8	1.26	0.83
16	30.75	0.00348	266.0	1.26	0.83
17	29	0.00286	214.0	1.40	0.80
19	26.5	0.00315	234.8	1.40	0.83
20	24.25	0.00096	56.6	1.68	0.82
21	22	0.00285	229.3	1.26	0.82
22	17.5	0.00274	231.6	1.26	0.79
23	15	0.00129	90.7	1.40	0.73
1	−4	0.00122	365.5	0.28	0.85
201	−110	0.00074	27.0	2.80	WR
202	−200	0.00047	118.9	0.42	WR
204	−270	0.00162	375.8	0.42	0.92
206	−470	0.00781	268.3	2.94	WR
HF–HCl residue					
192	1810	ND	5.6	ND	Residue
216	3115	0.00100	20.5	4.9	Residue

In all cases the evolved helium was purified and cryo-focused, separated from Ne at 32 K, and analyzed on a MAP 215-50 mass spectrometer using the usual procedures at Caltech [18]. For all samples the ^{4}He blank was insignificant ($\ll$1%). ^{3}He blanks were always <10% of the sample signal. Analytical uncertainty on peak height determinations for both isotopes is about 10%. The absolute detection limit, defined as 5× the background noise, is ~0.2 cps, which is equivalent to $\sim 3 \times 10^{-5}$ fmol of ^{3}He.

3. Results and interpretation

Results are shown in Table 1 and Fig. 1. ^{3}He concentrations are generally low, ranging from 0.0004 to 0.015 fmol/g. For comparison, a typical modern deep-sea carbonate yields about 0.02 fmol/g [19]. ^{3}He concentrations are lowest in the Permian part of the section, and then rise rapidly by about an order of magnitude through the PT boundary (Fig. 1a). Values at the boundary itself are not noticeably higher than elsewhere in the Triassic. As shown in Fig. 2, the ^{3}He concentrations covary with both Li concentration and total organic carbon concentration. ^{3}He/^{4}He ratios range from 1×10^{-8} to 7×10^{-8} with a weak suggestion of higher values in the Triassic part of the section (Fig. 1b).

There is no evidence for elevated ^{3}He levels at the PT boundary itself, located between 0 and 150 cm in Fig. 1. This observation is consistent with previous work on the Meishan and Shangsi PT sections [8] and in the Gartnerkofel core [16]. We thus continue to find no evidence for the fullerene-hosted ^{3}He reported [20] in PT sediments.

However, the data document a suggestive increase in ^{3}He concentration and ^{3}He/^{4}He ratio between the Permian and the Triassic. The key question is whether this rise reflects a change in the delivery rate of IDPs in association with some solar system event, or if instead it reflects a purely terrestrial phenomenon. There are three obvious possibilities: 1) the ^{3}He is not extrater-

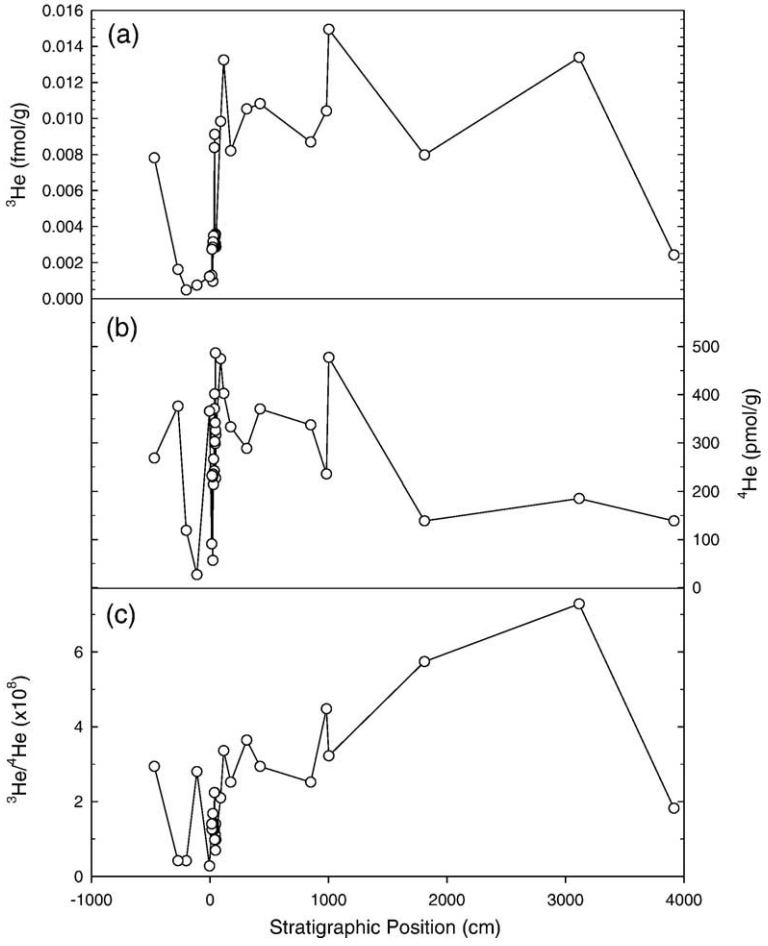

Fig. 1. (a) ^{3}He concentration, (b) ^{4}He concentration and (c) helium isotopic composition of Opal Creek samples.

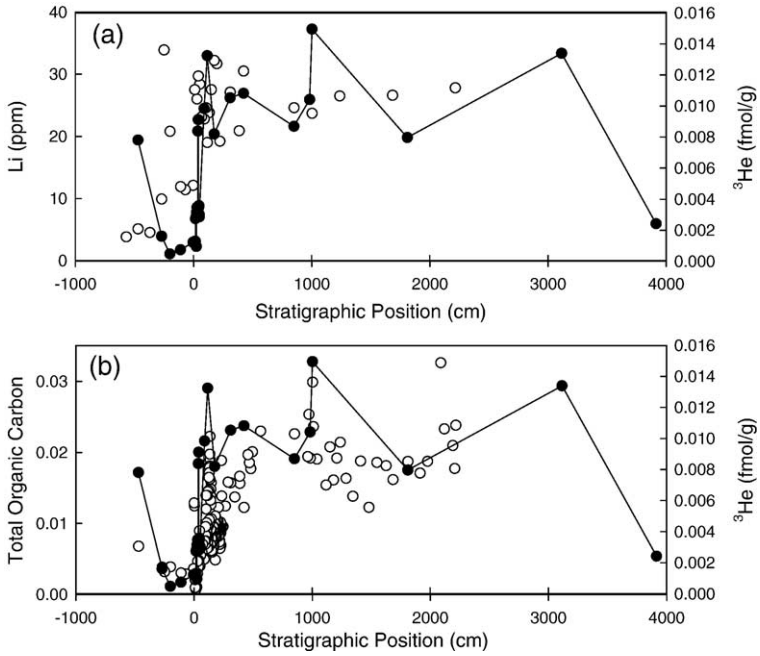

Fig. 2. Comparison of ^{3}He concentrations with (a) Li concentration and (b) total organic carbon fraction. Li and carbon data are from Garrison and Ward (unpublished).

restrial and the change in helium composition reflects variations in the abundance of terrestrial nucleogenic ^{3}He; 2) the ^{3}He is extraterrestrial and the variation in composition reflects changes in sediment accumulation rate; and 3) the change reflects real variation in IDP delivery rate.

Identification of extraterrestrial ^{3}He is usually possible using the He isotopic ratio. The ^{3}He/^{4}He ratio of extraterrestrial matter including IDPs and supposed extraterrestrial fullerenes is higher than $\sim 10^{-4}$ [21,22]. In contrast, terrestrial helium produced by U and Th decay and the nucleogenic reaction ^{6}Li$(n,\alpha)^3$H$\rightarrow^3$He yields a ^{3}He/^{4}He ratio in the 10^{-8} range, depending on rock chemistry, especially Li content [23]. This extreme isotopic contrast permits detection and quantification of extraterrestrial ^{3}He in many types of sediment, in which the measured ^{3}He/^{4}He ratio is higher than $\sim 10^{-7}$ [19]. However, in the Opal Creek sediments the ^{3}He/^{4}He ratios are all lower than this value, and are instead in the range of purely terrestrial helium. In the absence of detailed chemical analyses the production ratio in these samples is not well known, so it is impossible to confidently say whether extraterrestrial helium is present or not. This problem is not unexpected given the great age (and hence abundant radiogenic He) of these rocks compared to the more commonly analyzed younger sediments.

A second method for establishing the presence of extraterrestrial ^{3}He is to analyze the magnetic fraction of the sample. In many cases the magnetic material is highly enriched in ^{3}He and has a high ^{3}He/^{4}He ratio because IDPs tend to be magnetic [4,19,24]. However, attempts to extract a magnetic fraction from the Opal Creek samples failed — we found no separable magnetic material in these rocks.

As a final alternative we can take advantage of the unusually high release temperature of IDP-hosted ^{3}He [19,25]. For example, previous studies show that most IDP ^{3}He is released at temperatures in excess of 800 °C when heated in 1 h increments (Fig. 3b). We step-heated one of the most ^{3}He-rich of the Opal Creek samples (OC-216), and found that ^{3}He release is very strongly peaked at 650 °C, just slightly hotter than the peak ^{4}He release and lower than the expected IDP ^{3}He release (Table 2). Coupled with the low ^{3}He/^{4}He ratios these data provide strong evidence that the ^{3}He we are detecting is *not* hosted in IDPs.

Of potential interest is that the thermal release pattern from this sample is rather similar to that ascribed to fullerenes (Fig. 3a). For example, purported fullerene extracts from the Sudbury impact structure release most of their helium between 500 and 800 °C [21]. One possible interpretation of our observation of peak release at 650 °C is that ^{3}He (possibly extraterrestrial) is hosted in fullerenes rather than in IDPs. In further

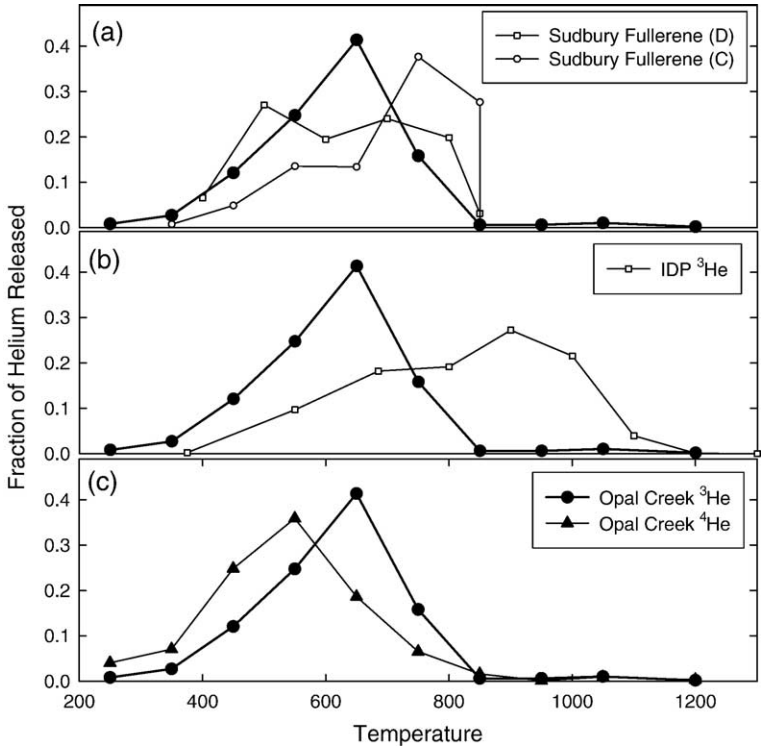

Fig. 3. Incremental step-heating release spectra for (a) ^{3}He in Sudbury fullerene (C=Capreol, D=Dowling) [21]; (b) ^{3}He in IDPs [19]; and (c) ^{3}He and ^{4}He in sample OC-216. In each panel the ^{3}He pattern for OC-216 is repeated for comparison. Note that ^{3}He from Opal Creek is released at temperatures significantly lower than found for IDPs, but in the range reported for fullerenes.

support of this possibility we note that He is well-correlated with total organic carbon content at Opal Creek (Figs. 2b and 4a) and that carbon-rich PT sediments are claimed to host extraterrestrial fullerenes [3].

To test this possibility, two ^{3}He-rich samples were subjected to an HF–HCl attack. This treatment dissolves most minerals but leaves fullerenes [21] and possibly other organic and/or carbonaceous molecules intact. After attack the residue was analyzed for helium just like the untreated samples. As shown in Table 1, the results of this experiment unambiguously demonstrate that ^{3}He *does not* survive this treatment. All of these observations support the interpretation that there is no detectable extraterrestrial ^{3}He in the Opal Creek samples, neither in IDPs nor in fullerene.

Table 2
Results of step heating of sample OC-216

Temperature (°C)	^{3}He (fmol/g)	^{4}He (pmol/g)	^{3}He/^{4}He ($\times 10^8$)	Fraction ^{3}He	Fraction ^{4}He
250	0.00017	12.41	1.388	0.008	0.040
350	0.00056	21.72	2.576	0.027	0.071
450	0.00250	76.15	3.279	0.121	0.248
550	0.00512	110.09	4.653	0.247	0.359
650	0.00857	57.18	14.983	0.414	0.186
750	0.00327	20.00	16.355	0.158	0.065
850	0.00013	4.88	2.645	0.006	0.016
950	0.00013	0.43	30.117	0.006	0.001
1050	0.00022	2.81	7.653	0.010	0.009
1200	0.00004	1.10	3.921	0.002	0.004

4. Discussion

4.1. Variation in non-extraterrestrial ^{3}He concentration

If the measured ^{3}He is purely terrestrial, why does it show a large increase in concentration at the PT boundary? This boundary is slightly above a major lithologic break, from cherts in the Permian to siltstones and shales in the Triassic. As a result there is a large change in rock chemistry corresponding to the change in ^{3}He. The simplest explanation for the increase in ^{3}He is the increase in Li concentration from Permian to Triassic. Indeed an ~5× increase in Li concentration occurs at about the same stratigraphic position as the ^{3}He increase (Fig. 2a). However, in detail the ^{3}He and Li concentrations are not well correlated (Fig. 4a), yielding an insignificant r^2 correlation coefficient of <0.01.

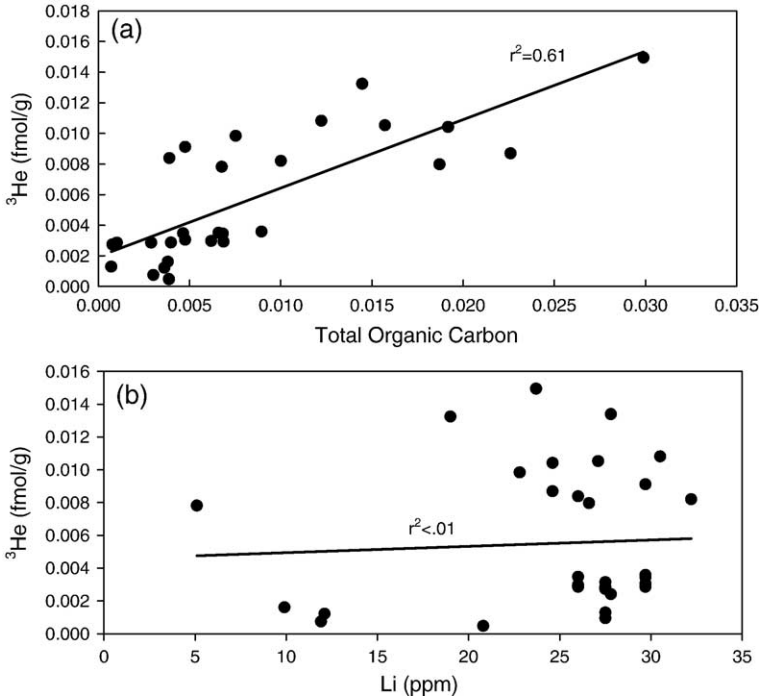

Fig. 4. Relationship between ^{3}He and (a) total organic carbon fraction and (b) Li concentration. A regression line and correlation coefficient are shown for each plot. The correlation with ^{3}He is far better for organic carbon than for Li concentration. Li and organic carbon data are from Garrison and Ward (unpublished).

This lack of correlation indicates that other factors must be involved.

The lithologic and ^{3}He contrast also correspond to a dramatic increase in total organic carbon content (Fig. 2b). Unlike Li concentration, there is a significant correlation between organic carbon and ^{3}He ($r^2=0.61$). At present we have no straightforward explanation for this relationship, although we note that our experiments rule out the possibility that ^{3}He is trapped in acid-resistant carbonaceous matter like fullerenes. The presence of higher concentrations of U and Th in the organic-rich part of the section, and probable correlated variations in the concentrations of trace elements with high-neutron absorption cross-sections (e.g., B, Gd) may be involved.

4.2. Comparison of Opal Creek with other PT boundary sections

Fig. 5 is a compilation of helium isotope measurements from Permian–Triassic boundary sections around the world, plotted as ^{3}He concentration as a function of ^{4}He concentration. The plot includes both whole rock and magnetic fraction data. A striking feature of this figure is that *every* sample reported by the Becker group [3,4] from Meishan, Sasayama and Graphite Peak (Antarctica) lies to the high-^{3}He side of the maximum radiogenic production ratio (solid line, ^{3}He/^{4}He = 6×10^{-8}; [19]), demanding the presence of an additional, presumably extraterrestrial, component. In contrast, *every* Permian–Triassic age sample analyzed at Caltech, from Opal Creek, the Garnterkofel core [16], and Meishan and Shangsi, China [8] plots at or below the maximum production ratio. This discrepancy demands explanation.

The apparent absence of extraterrestrial ^{3}He in the Caltech samples is initially surprising because these rocks are expected to have at least some extraterrestrial helium from the accretion of IDPs. These sections accumulated at rates [3,16,17] similar to modern sediments in which IDP ^{3}He is readily detected [19], so simple dilution by rapid sedimentation is not a likely explanation. Diffusive helium loss is an alternative possibility. To characterize helium loss from sedimentary IDPs, Mukhopadhyay [26] performed detailed step-heating experiments on Cenozoic-age sediments. Representative Arrhenius plots for extraterrestrial helium diffusion from bulk sediment and a magnetic separate from his work are shown in Fig. 6. Also plotted are diffusion coefficients computed from the step heat data reported by Poreda and Becker [4] on magnetic separates from Graphite Peak. Diffusion kinetics from

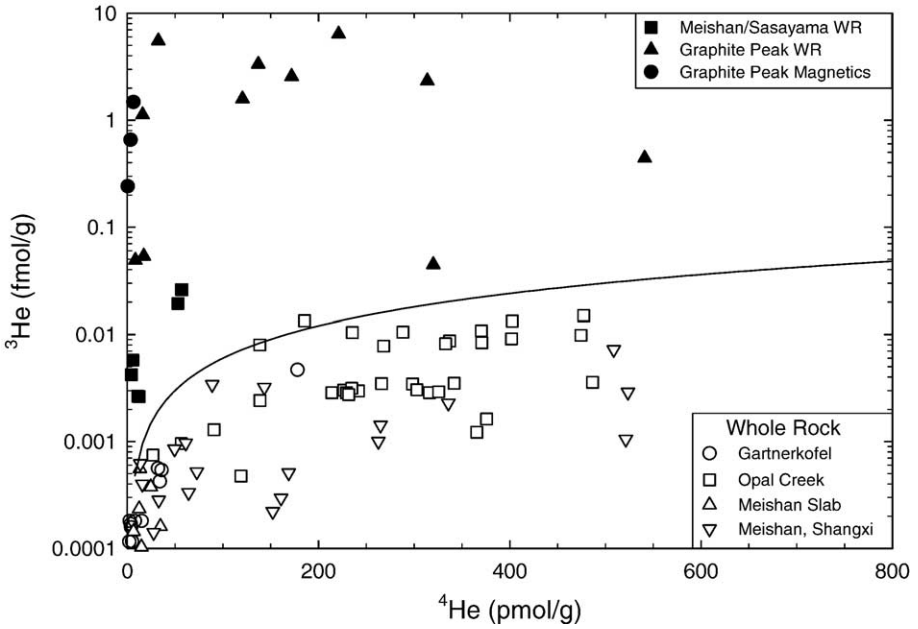

Fig. 5. Compilation of He isotope data from sedimentary rocks from at and near the PT boundary. There is a striking distinction between all measurements made at Caltech (open symbols) and all measurements reported by the Becker group [3,4]. The Caltech samples have ^{3}He/^{4}He ratios lower than a reasonable upper limit of the nuclear production ratio (solid line, 6×10^{-8}) and thus provide no evidence for extraterrestrial helium. In contrast the Becker group samples [3,4] lie on the high-^{3}He side of nuclear production, requiring an extraterrestrial component. Data sources for open symbols: [8,16], Table 1, and Farley unpublished.

the PT age Graphite Peak rocks and the Cenozoic age sediments are in remarkable agreement. In accord with the conclusions of Poreda and Becker [4], this similarity provides evidence that the Graphite Peak ^{3}He is dominantly hosted in the same phase that hosts ^{3}He in modern sediments: IDPs.

Based on these diffusion data, Mukhopadhyay [26] concluded that even modest burial heating can cause substantial diffusive helium loss from IDPs in sediments. For example, >90% helium loss will occur at temperatures in excess of 70 °C when held for millions of years. Tools commonly used to assess sediment heating are not very sensitive to such a low temperature. For example, at Meishan and Shangsi, conodont alteration indices of 1 to 1.5 suggest maximum temperatures below 100 °C (Ian Metcalf, personal communication, 2004), but do not rule out temperatures above 70 °C. Thus it seems at least possible that the absence of extraterrestrial ^{3}He in the Caltech samples is simply a result of deep burial and heating of these old rocks. Indeed, with the exception of a very unusual period of high extraterrestrial flux in the Ordovician [27] and the PT samples of Poreda and Becker [4] and Becker et al. [20], extraterrestrial helium has not been detected in samples older than ~150 Ma (Farley, unpublished data), probably for this reason.

If this is the correct explanation for the absence of extraterrestrial helium in the Caltech samples, then Fig. 5 would imply that the samples analyzed by Poreda and Becker [4] and Becker et al. [20] are from sections subjected to lower degrees of burial metamorphism. This is clearly not the case for the Meishan samples, which are reported to carry extraterrestrial helium despite the fact that they are from precisely the same locality as the barren samples analyzed at Caltech [8]. Becker and Poreda [28] propose that this discrepancy arises from sample heterogeneity. However, in the case of Graphite Peak, there is strong evidence for heating to temperatures far above those required for total ^{3}He loss, so the presence of extraterrestrial helium there is not easily rationalized.

Based on the general stratigraphy of the Beardmore Glacier region of the Transantarctic Mountains [29], the Graphite Peak PT samples were buried by approximately 1.3 km of Triassic sandstones and tuffs of the Beacon Supergroup, followed by perhaps 700 m of Jurassic volcanics. The most notable phase of volcanism occurred during rifting of Gondwana [29], and culminated with intrusion of voluminous sills of Ferrar dolerite and eruption of the associated up to 400 m thick Kirkpatrick basalts at ~180 Ma [30]. It is clear that this rifting was associated with extensive heating of Beacon Super-

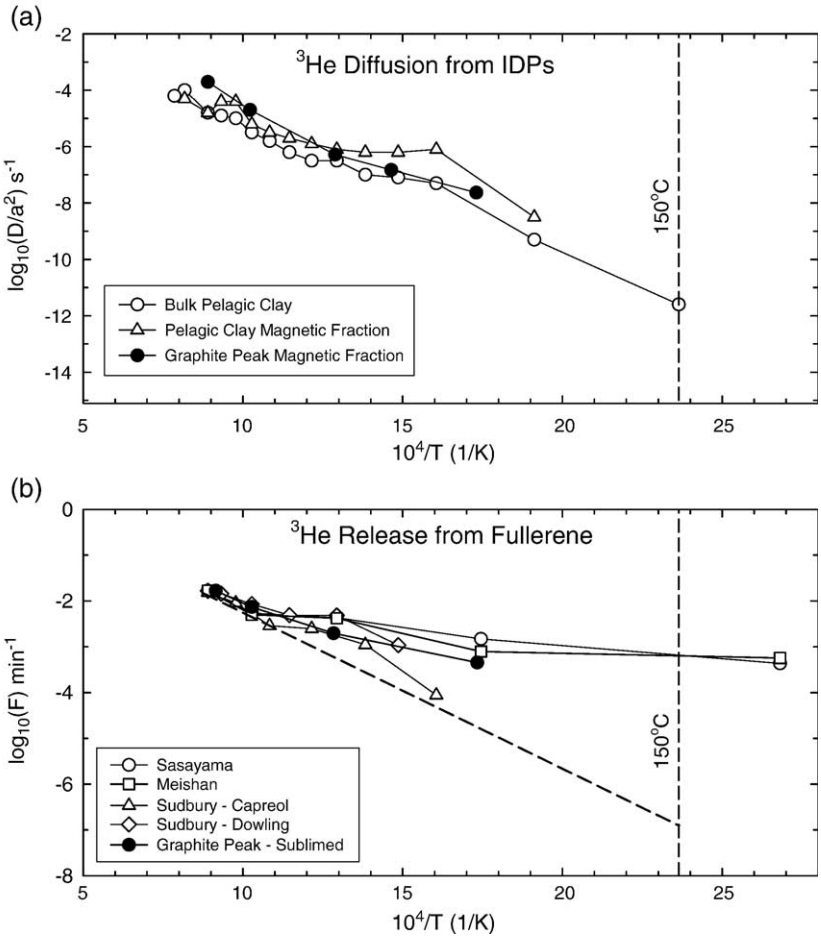

Fig. 6. Kinetics of extraterrestrial helium release from IDPs and fullerene. (a) ^{3}He diffusion from Cenozoic-age bulk sediment and magnetic fines [26] and computed from the Graphite Peak magnetic fraction step heat data of [4]. All three plot on similar Arrhenius arrays and are consistent with ^{3}He being hosted in IDPs. Vertical dashed line indicates conservative estimate of maximum temperature experienced in Graphite Peak section. (b) ^{3}He release rate from fullerene extracted from sediments [4,20,21]. *F* is fractional He release per unit time, see [20]. Note that the vacuum-sublimed Graphite Peak fullerenes do not yield higher He retentivities than non-sublimed samples, suggesting that trace solvents do not greatly modify helium release. Sloping line indicates reasonable lower bound of He release rate.

group rocks. For example, Barrett et al. [29] estimate that the entire formation that includes the PT boundary was heated to between 200 and 300 °C, with some portions heated even more intensely as a result of their proximity to Ferrar sills. Similarly, the PT boundary at Graphite Peak is located a few cm above a coal bed. Although the rank of this coal has apparently not been described, the large number of coals described from the Beacon Supergroup in general and from the Beardmore Glacier region in particular range from low volatile bituminous to anthracite [31]. Based on the relationship between coal rank and vitrinite reflectance [32], and between vitrinite reflectance and temperature [33], these coals indicate temperatures likely exceeding 200 °C for at least hundreds of kyrs.

The implications of this heating are profound and cast doubt on the published interpretation of the helium isotope results from Graphite Peak [4,20]. We conservatively assume the PT samples reached 150 °C, i.e., 50 to 150 °C lower than previous estimates [29]. As shown in Fig. 6a, the helium diffusivity from interplanetary dust particles at this temperature is $\sim 10^{-11.6}$ s^{-1}. Note that this diffusivity was actually measured, so no extrapolation along the Arrhenius trend is required. Using standard diffusive loss equations [34], we calculate that at this temperature 99.999% helium loss is expected in 16 kyrs, and 99% loss in just 9 kyrs. Thus massive helium loss from IDPs is expected in samples of the Beacon Supergroup at Graphite Peak.

One might hypothesize that massive loss of extraterrestrial ^{3}He has occurred from these rocks, and that

high extraterrestrial helium concentrations are nevertheless observed [4] because the IDP abundances are extraordinarily high, perhaps thousands of times higher than observed in modern pelagic clays [35]. However, this raises a different problem. Based on the He and Ne diffusion kinetics reported by Hiyagon [25] on modern IDPs (obtained by collection of magnetic fines from pelagic clays), the diffusivities of extraterrestrial He and Ne differ by about a factor of 1000 when extrapolated to 150 °C. If this extrapolation is accurate, then IDPs which have lost 99.999% and 99% of their helium should have $^{21}Ne/^{4}He$ ratios enriched by factors $>10^4$ and 100, respectively. Yet Poreda and Becker [4] report $^{21}Ne/^{4}He$ ratios in Graphite Peak magnetic fractions that are within an order of magnitude of those found in unheated modern deep-sea magnetic fines. Unless the diffusivity parameters proposed by Hiyagon [25] are, for some reason, invalid, the Graphite Peak samples show no evidence for the expected extent of helium loss and associated He/Ne fractionation.

The situation for fullerene appears to be similar. The temperature dependence of helium release rate from natural "extraterrestrial" fullerenes from several localities has been reported [20,21], including from Graphite Peak [4]. Following these authors, the results are reported as fractional helium loss rate as a function of reciprocal temperature in Fig. 6b. An Arrhenius-type relationship is expected if the "opening" of fullerenes is a thermally activated process. For unknown reasons, the published results do not form a tightly linear Arrhenius relation in Fig. 6b. However, the maximum retentivity consistent with the data can be estimated by projecting a line through the most retentive steps (dashed line in Fig. 6b). At 150 °C, the implied fractional loss rate is 13.2%/yr. At this rate 99.999% He loss is expected in <100 yrs! It has been suggested that the solvents used to extract fullerenes may accelerate He release [36], so the rates in Fig. 6b may be inapplicable in nature. However, we note that the Graphite Peak measurements reported by Poreda and Becker [4] were obtained on fullerenes that were purified by vacuum sublimation. Despite this analytical step, which should have removed a very large fraction of the solvent, the release rates are indistinguishable from previously published measurements made on fullerenes that were apparently not purified in this way. Thus there is no evidence that solvents are responsible for the low retentivity implied by Fig. 6b. Furthermore, even air is thought to catalyze fullerene opening [36], and air was very likely present in contact with the PT samples. Experiments to assess fullerene He loss rates under appropriate in situ conditions are required, but retentivity would have to be many orders of magnitude higher than implied by the vacuum heating experiments for helium to be retained in the Graphite Peak PT section.

Taken together these observations seem to require one of three possible solutions: 1) the PT sections with extraterrestrial helium were not heated to the temperatures implied by geologic constraints; 2) the carrier phases of extraterrestrial helium are more retentive than presently thought; or 3) the extraterrestrial component was not present in the PT samples during peak burial heating. The first explanation is hard to accept given the strong geological evidence of heating at Graphite Peak based on metamorphic petrology and kerogen maturation and from reasonable predictions of the thermal consequences of Gondwana break-up volcanism. A more retentive helium carrier phase in PT samples compared with Cenozoic age sediments is perhaps possible, but direct measurements on Graphite Peak PT age samples do not support this explanation (Fig. 6).

The final possibility – contamination by younger material – bears examination. It is well known that polar ice, especially in zones of ablation, can have high concentrations of IDPs and of micrometeorites [37,38]. This extraterrestrial material could conceivably be blown from the ice to the Graphite Peak outcrop. Although this may seem implausible, a very similar possibility has been hotly debated for the origin of microfossils in Sirius Group tillites elsewhere in Antarctica: are the microfossils indigenous, or were they deposited later by winds (see, e.g., [39])? Highly porous or fractured rock would favor this possibility, but no details on the physical character of the samples analyzed for fullerenes and IDPs were reported [4]. In principle this question can be resolved by analysis of core samples or by careful surface cleaning of large outcrop samples prior to analysis, but such samples apparently do not exist.

5. Conclusions

A high resolution study of helium isotopes across the Opal Creek PT boundary section provides no evidence for extraterrestrial ^{3}He. These observations are fully consistent with similar negative results from the Meishan and Shangsi [8] and Gartnerkofel sections [16]. In themselves these observations do not rule out an extraterrestrial impact at the PT boundary. Failure to detect extraterrestrial ^{3}He could occur because the analyzed samples happened to miss an impactoclastic layer [28], or because the rocks of these sections have experienced sufficiently intense diagenesis to release

their original burden of extraterrestrial ^{3}He [26], or because the impact event did not enhance the ^{3}He flux. However, these observations stand in stark contrast to previous studies by a single group [3,4] favoring a PT impact based in part on the detection of extraterrestrial ^{3}He at several sections.

If extraterrestrial ^{3}He is indeed present at the PT boundary, it must be highly heterogeneously distributed. Alternatively, given the strong geologic and laboratory-based data suggesting near complete extraterrestrial He loss and extensive He/Ne fractionation from Graphite Peak samples which nevertheless are reported to carry nearly pristine extraterrestrial noble gases, it would seem prudent to treat the evidence for an extraterrestrial component as a potential contaminant until proven otherwise.

Although we detected no extraterrestrial ^{3}He at Opal Creek, there is a strong increase in ^{3}He concentration across the PT boundary. This variation likely arises because of enhanced production or retention of nucleogenic ^{3}He in the Li and organic carbon-rich sediments of the Triassic relative to the Permian. Careful study is required to distinguish these purely terrestrial effects from real changes in the flux of ^{3}He from space.

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