PLANETARY GASES AND FULLERENES AT THE PERMIAN-TRIASSIC BOUNDARY. Luann Becker1 and Robert J. Poreda2, 1Department of Earth & Space Sciences, University of Washington, Seattle, WA 98195 email: lbeck00@u.washington.edu; Department of Earth & Environmental Sciences, Rochester University, Rochester, NY 14626

Introduction: The extinction event that marks the Permian-Triassic boundary (PTB) (251.4 ± 0.3 Ma) was the most severe in the last 540 Ma, killing off over 90% of all marine species, ~70% of terrestrial vertebrate genera, and most land plants [1]. Several new studies have shown that these extinctions were much more abrupt than previously thought, with estimates of the extinction interval ranging from <500,000 years [2] to ~8,000 years [3]. Proposed catastrophic hypotheses for the PTB extinction event include bolide impact (asteroidal or cometary) [4] and/or massive flood basalt volcanism [5]. Radiometric ages of the Siberian Flood Basalt volcanism (251.2 ± 0.3) [2,5] suggest that the volcanism is coincident with the time of the PTB extinction event. Other extinction mechanisms involving ocean anoxia, and changes in sea level and climate have also been proposed [1].

The suggestion by Alvarez et al., [6] that bolide impact was the ultimate reason for the mass extinction observed at the 65 myr Cretaceous/Tertiary boundary (KTB), led to the assumption that all such events were associated with extraterrestrial (ET) cause. Despite a compelling scenario developed for the KTB (e.g. iridium, shocked quartz, microspherules), the case for the PTB mass extinction remains unresolved. One of the problems with an extra-terrestrial (ET) trigger for the PTB event is that there exists no significant iridium (Ir) anomaly at the PTB [6] that is comparable to KTB enrichments of 10 to 100 times above background. Here, we report that some PTB sediments contain fullerenes with trapped noble gases that are indicative of an extraterrestrial source.

Fullerenes have been previously associated with two separate impact events involving a large bolide with the Earth in the 1.85 billion-year-old carbon-rich breccias (Onaping Formation) at the Sudbury Crater (7) and in clay sediments from the 65 million-year-old KTB layer [8]. The fullerenes in both deposits contain noble gases encapsulated within the cage of the fullerene molecules [9]. The isotopic compositions of the gases are similar to those found in meteorites and some interplanetary dust particles (IDPs) but are unlike that of the Earth’s atmosphere. To provide the link between fullerenes in impact deposits and the bolide itself, fullerenes (C60 to C70) have now been isolated from the Murchison and Allende carbonaceous chondrites with He and Ar isotopic ratios that can only be explained as extraterrestrial in origin [9]. Based on these findings, fullerenes appear to form in an ET environment, are exogenously delivered to the Earth in some meteorites or comets and are preserved in impact deposits associated with a major extinction event.

Fullerenes (C60 and C70) have been reported in PTB sediments from Inuyama, Central Japan [10], and is linked to extensive wildfires [8] on the supercontinent Pangea and subsequent deposition on an anoxic deep-sea floor of the superocean Panthalassa. However, unlike the KTB, the PTB has no corresponding soot material within the boundary layer, diagnostic of biomass burning triggered by the impact event [11]. In this study, we measured the isotopic compositions of the encapsulated noble gases to determine the environment of fullerene formation [9]. The fullerene spectrum and encapsulated noble gases were examined in sediments from three PTB locations: the classic PTB section at Meishan, South China; the Sasayama section, Southwest Japan and the Bálvány section, Bükk mountains in Northern Hungary.

LDMS Analyses: The sediment samples were demineralized and extracted with organic solvents (e.g. toluene) [9]. Laser desorption mass spectrometry (LDMS) analysis of the toluene extract for the Meishan, China sediment showed a peak at a mass-to-charge ratio (m/z) of 720 atomic mass units (amu) that corresponds to C60+, and a peak at 840 amu, which corresponds to C70+ (~5 micrograms, µg). Similar results were obtained for the Sasayama sample, however no mass peaks corresponding to C60+ and C70+ were detected in the Bálvány, Hungary toluene extract (i.e. < 50 ng or 1 ppb). LDMS analyses of the 1,2,3,5 tetra-methyl benzene (TMB) Meishan fullerene extract (~14 µg) residue revealed a small mass peak for C60 and a much more prominent high-mass envelope that dominates the spectrum between C70+ and C90+. These higher fullerene-related carbon (C) clusters are separated by 24 amu or a C2+ ion, which is a diagnostic indicator that the high-mass envelope detected in the TMB residue is composed of pure C clusters rather than some other molecule or compound [9]. Moreover, no fullerenes were detected in beds 33 and 17 above and below the Meishan, PTB.

The TMB extract for Sasayama (~10 µg), displayed much more prominent mass peaks for C60+ and C70+ and a limited series of higher fullerenes between (C50+ and C40+). We attribute the lower abundance of higher fullerenes to degradation in the Sasayama PTB sediments, possibly a result of later tectonism. Sediment residues from the cherts above and below the PTB layer have fullerenes at or below the blank (50 ng, or 1 ppb), suggesting that the fullerene signal is recording a short-term event rather than the continuous deposition of interplanetary dust particles or IDPs to the sediments [12]. The TMB extract from the Bálvány, Hungary PTB indicated a weak signal for C60+, C70+ and some higher fullerenes, however, the yield of fullerene was extremely low (~1 µg). Samples of limestones above and below this layer were also devoid of fullerene (<50 ng or 1 ppb). Either the environment of deposition and/or subsequent geologic processing over some 250 myrs was not conducive to fullerene preservation at Bálvány, or the sediment layer examined in this study is not at the PTB.

Noble Gas Analyses: The helium isotopic composition of fullerenes from both the Meishan and Sasayama PTB boundary sites are within the range reported for the “planetary” component in meteorites (~1.4 x 10−6) [13]. The total helium concentrations in the two PTB boundary samples are also similar (0.1 to 0.2 µ cc 3He/g) and equivalent to the Sudbury fullerenes [7]. The ET signature of the helium provides strong evidence that the
PTB fullerenes were delivered intact to the Earth in a bolide (asteroidal or cometary) at the PTB. To confirm that the increase in the fullerene component at the PTB results from an impact and not from a change in the sedimentation rate at the boundary, we examined the $^3$He concentration in the bulk Sasayama sediments at several intervals. At Sasayama, the bulk $^3$He actually decreases at the boundary, while the fullerene and the “fullerene encapsulated $^3$He” concentrations increase more than 50-fold. The “fullerene encapsulated $^3$He” represents almost 50% of the total $^3$He in the bulk sediments as opposed to ~1% above and below the boundary. The magnitude of this unique $^3$He signal at the boundary points to a discrete event, in contrast to the continuous IDP source to the deep-sea sediments [12].

In support of the hypothesis that a “planetary” gas reservoir existed at the time of fullerene formation (as opposed to a “solar” gas reservoir), the ratio of $^3$He/$^{36}$Ar resembles most closely the “planetary” ratio (Fig. 1) present in carbonaceous chondrites [13,14]. The measured $^{36}$Ar/$^{36}$Ar ratios are 70 to 220 and the $^{36}$Ar in the fractions is between 75 and 25% “planetary gas” with an atmospheric $^{38}$Ar/$^{36}$Ar ratio, also consistent with a planetary signature. The data falls off the “perfect” air-“planetary-gas” mixing line due to preferential release of He relative to Ar during extraction. Mixing with a “solar” gas component ($^3$He/$^{36}$Ar ~1) clearly does not fit the measured He-Ar isotopic systematics. The neon isotopic ratios also support a planetary gas reservoir, although the evidence is not as strong.

Because of the known property of fullerenes to incorporate noble gases as a direct function of the partial pressure of the gas (i.e. rigid sphere model), the data suggests a partial pressure in the environment of formation equivalent to ~2 to 4 torr of He. Only stars or collapsing gas clouds (8) have significant helium pressures and provide an environment of formation conducive to fullerene synthesis (i.e. low H/C ratios). Overall, the light noble gas data for two PTB deposits and the Murchison carbonaceous chondrite show consistent results that point to a “planetary” gas reservoir at the time of fullerene formation [13,14].

Synthesis of fullerenes during impacts on Earth or in space would not lead to high noble gas concentrations with this distinctively planetary, chemical and isotopic signature. This planetary signature dominates the noble gas isotopic composition of the PTB sediments and the carbonaceous acid-residue for Allende and Murchison, although the yields of the fullerene carrier phase are much lower.

Thus, it would appear that extraterrestrial fullerenes were delivered to the Earth at the PTB possibly related to a cometary or asteroidal impact event. Such an event could have caused the severe end-Permian mass extinction. Our results are consistent with recent paleontological studies that now point to a very rapid extinction event. The unique planetary signature measured in fullerenes isolated from the Murchison carbonaceous chondrite and the PTB sediments demonstrates that this distinctive noble gas carrier can survive major impact events and contribute to the unique gas signature of the terrestrial planetary atmospheres.