Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary

Light Noble Gases in the Geological Mass Extinction Layers in Hungary

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The elemental abundance and isotopic ratio of He and Ar have been measured in the sedimentary rock samples of Permian (P) - Triassic (T) and Triassic (T) - Jurassic (J) boundary layers in Hungary. Low $^{3}He/^{4}He$ and high $^{40}Ar/^{36}Ar$ ratios as compared to the air values have been found, suggesting that radiogenic components are predominant in these layers. The $^{38}Ar/^{36}Ar$ ratios are also atmospheric. Thus, it is likely that all these isotopic ratios of noble gases are not indicating an extraterrestrial impact. However, there seems to be pulse increases of ^{3}He concentration at the P- T boundary compared to other P and T samples. This still maintains the possibility that an extraterrestrial input is the cause for the mass extinction at the P- T boundary.

Keywords: sedimentary rock, $^{38}Ar/^{36}Ar$ ratios, radiogenic components, noble gases

On the Earth, severe mass extinctions have occurred five times during the past about 540 million years (My). They are the *Five Big Extinctions* and have occurred at the Late Oldovician (~435 million years ago (Ma)), Late Devonian (~360Ma), Permian--Triassic boundary (~245Ma), Triassic-Jurassic boundary (~205Ma), and Cretaceous--Tertiary boundary (~65Ma). These events were probably triggered by global environmental changes leading to the extermination of more than 70% of the living world. It was reported that an Ir anomaly was found in the Cretaceous--Tertiary (K-T) boundary and that the cause of that mass extinction (mainly of the Dinosauriers) was an extraterrestrial event [1]. Other evidences of the extraterrestrial impact have been discovered for the K - T boundary. Thereafter, many scientists have tried to find the evidences of extraterrestrial impact for other mass extinction events [e.g. Ref. 2].

The Permian-Triassic (P- T) boundary event has been the most severe one in the *Big Five*. More than 90% of whole lives on the Earth (marine fixed species, terrestrial vertebrates, and plants etc.) had been wiped out from the Earth within a short period of time [e.g. Ref. 3]. However there has been no established evidence of the extraterrestrial evidence at the P- T boundary. Deciphering the cause of this mass extinction event has been one of the central issues in the geosciences. Noble gases, being chemically inert and having several isotopically distinct ratios among terrestrial and extraterrestrial materials have been providing crucial (and controversial) information regarding the issue [4-6]. A recent discussion over the cause of the mass extinction at the P- T boundary initiated by the exciting report of high $^{3}He/^{4}He$ ratio in fullerenes supposedly recovered from the P- T boundary [7] from which an extraterrestrial cause (i.e., an impact event) of the P- T mass extinction was advocated. However, this finding was questioned [6] by many authors [8] based on experimental and other arguments [9]. Recently [10] reported that they found chondritic meteorite fragments from the P- T boundary of Antarctica.

So far, no conclusive explanation has been given for the cause of the P-T event based on noble gas information, despite the general expectation that the noble gases can be used as good tracers of extraterrestrial contributions to the understanding of mass extinction events. Thus, we believe that it is very important to provide comprehensive noble gas data from well-characterized geochemical boundary sections for a more conclusive explanation of the cause of the P-T catastrophe; this would help to discriminate the impact hypothesis from other widely advocated models such as the anoxic event [11]. Here we report our preliminary results of new measurements of noble gases of sedimentary rocks collected from four sections in Hungary including the P- T and T-J boundaries.

Samples and sample preparation

Samples of thirteen sedimentary rocks were collected from four sections in Hungary.

Csövár north of Budapest (CS 1 to CS3, and CS41), Balatonarács in West Hungary (BA1-6), Kemesnye (BKl to BK4) and Bálvány (BBl to BB4) in the Bükk mountains (fig. 1). CS 1 consists of limestone enriched in spherules at the T-J boundary layer, two rock samples below the boundary were labelled CS2 and CS3, respectively, which consisted of limestone and chert. CS41 was sampled near the sampling place of CS1 to CS3. The sampling was from the lithological boundary of which uncertainty is about ~±10cm of the boundary. BA1-6 of red sandstone was collected below 30cm the P- T boundary and contains a large amount of spherules.

A sequence of black limestone samples were collected from the P-T boundary in the Bükk mountains: BK1 (30 cm below the boundary), BK2 (just at the boundary), BK3 (40cm above), and BK4 (85cm above). The late Permian layer is composed of black limestone with brachiopods and crinoideans. These sampling positions have uncertainties of ~±5cm and the width of each is about 5cm. For the BB series, BB2 consists of reddish clay enriched spherules at the P-T boundary. BB1 was picked up at the site 5cm lower than BB2 and consists of black limestone. BB3 and BB4 were above 60cm and 140cm the boundary, respectively. They contain clay and carbonate rich marl.

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Fig.1. The map of Hungary. Solid squares indicate the sampling sections

Samples weighing 40~80g (table 1) were loaded into 100ml beakers and baked at 110°C for about one hour to evaporate water contained in the rocks. Then all of them were repeatedly treated with 1N-HCl at room temperature in order to remove $CaC0_3$. They were rinsed with distilled water and baked twice at 120°C for about one hour to assure dryness. The ratios of the acid residue to original rock were various from a few to about 90 percentage by weight (table 1).

Table 1

PREPARATION OF THE SEDIMENTARY SAMPLES

Sample	Original amount [g]	Amount of residue [g]	Concentration factor
T-J section samples			
CS1	45.680	8.475	5.39
CS2	44.535	8.605	5.18
CS3	42.930	34.620	1.24
CS41	47.140	8.025	5.87
P-T section samples			
BA1-6	47.020	42.815	1.10
BK1	36.570	2.520	14.51
BK2	45.355	11.670	3.89
BK3	53.675	6.735	7.97
BK4	74.525	3.340	22.31
BB1	78.895	30.450	2.59
BB2	43.745	4.015	10.90
BB3	36.755	2.950	12.46
BB4	34.135	4.515	7.56

Noble gas analyses

We used a sector-type mass spectrometer with a double collector VG5400 installed at Osaka University. Samples were weighted and wrapped in aluminum foil, then mounted in the sample holder of the extraction furnace and kept in vacuum for about 10 h. Each of them was loaded in a molybdenum crucible in the furnace. Helium and argon gases were extracted from the sample by a single step heating at 1600°C with a tantalum heater. The extracted gas was purified by a Ti-Zr getter heated at about 700°C for 15min to remove the active gas, and cooled for 10 min. After the first purification, the remaining gas was purified again by a second Ti-Zr getter at the same temperature and time. The gases except for He were trapped by a cryogenic trap at 18K (-255°C) for 20 min. The helium gas was passed through activated carbon at liquid nitrogen temperature (~-196°C) for 10 min to trap remaining HD and heavier gases. The gas was introduced into the mass spectrometer for the measurement of the He abundance and isotopic ratio. In order to reduce HD, the gas was exposed to the second cold trap during the He analysis. After the He analysis, Ar was released at 75K (-198°C) for 20min and introduced into the mass spectrometer. For ^{4}He and ^{40}Ar a Faraday collector and for others an electron multiplier were used.

In the measurement of hot blank the same procedure was used as that for samples without a sample in the furnace. The typical hot blanks were ~$2.5 \cdot 10^{-13}$, ~$2 \cdot 10^{-9}$, and ~$5 \cdot 10^{-10}$ cm^{3}STP for ^{3}He, ^{4}He, and ^{36}Ar, respectively.

Results and discussion

As listed in table 2, The P-T and T-J samples have a range of ^{4}He concentrations from 10^{-9} to 10^{-5} cm^{3}STP/g. Correspondingly, ^{3}He/^{4}He ratios varied nearly two orders of magnitude and were all lower than the atmospheric ratio of $1.399 \cdot 10^{-6}$. Our data clearly support previous results [9, 12]. There is a rough negative correlation between ^{3}He/^{4}He ratios and the ^{4}He concentration (fig. 3), indicating that in situ radiogenic ^{4}He is largely controlling the ^{3}He/^{4}He ratios of the samples. The presence of an in situ radiogenic noble gas component is also evident as their ^{40}Ar/^{36}Ar ratios of 1800 to 52000 are significantly larger than the atmospheric ratio of 295.5. Our preliminary XRF analyses on some of the samples showed about 10 % of K_2O contents, which corresponds to a K-Ar age of 2 to 12Ma. These are apparently shorter than the supposed sedimentation ages of the respective samples. The significance of this is not clear, but the gross loss of radiogenic ^{40}Ar at some stage in the past or recent addition of K to the samples is suggested. Although Ar isotopes were not measured [9] our results are quite different from [7] that found ^{40}Ar/^{36}Ar ratios lower than in air. Indeed, the sedimentary rocks can easily be contaminated by atmospheric noble gases during their sedimentation and subsequent alteration processes. These processes undoubtedly severely affect argon isotopes quite easily. In fact, our observed ^{38}Ar/^{36}Ar ratios are atmospheric within experimental uncertainties and showed no evidence for preservation of extraterrestrial argon, if any, in all samples (fig. 4). This does not suggest directly the absence of extraterrestrial material (having ^{38}Ar/^{36}Ar ~ 1.52) in the present samples; but that the addition of air-Ar is so significant that we cannot detect any other non-radiogenic argon component in them. Thus, only helium isotopes, which are significantly less susceptible to atmospheric contamination, can be useful to identify intrinsic isotope signatures.

However, as noted above, there is a significant contribution of radiogenic ^{4}He in all samples and the obtained ^{3}He/^{4}He ratios are much lower than those in the air. This implicitly suggests that observed ratios are the lower limits of the original ^{3}He/^{4}He ratios. The fact that the K-Ar system is significantly disturbed also indicates that the U-^{4}He system is largely disturbed as well. In such a case, any attempt to estimate the amount of radiogenic ^{4}He in each sample to calculate an original ^{3}He/^{4}He ratio would be impossible. Thus, hereafter, we use the absolute amount of ^{3}He as an indicator of extraterrestrial component, if any, in the samples.

The reason why we regard the concentration of ^{3}He to be useful is that those in the terrestrial surface materials are generally quite low. Possible processes to affect ^{3}He contents at the near surface include (1) an addition of the cosmogenically produced component, (2) a nucleogenically produced component by the ^{6}Li(n, α)3H$\rightarrow$^{3}He reaction, and (3) an extraterrestrial input with high ^{3}He concentration. Addition or production of ^{3}He by the above processes to originally ^{3}He-depleted material can be detected quite sensitively. It should be noted that

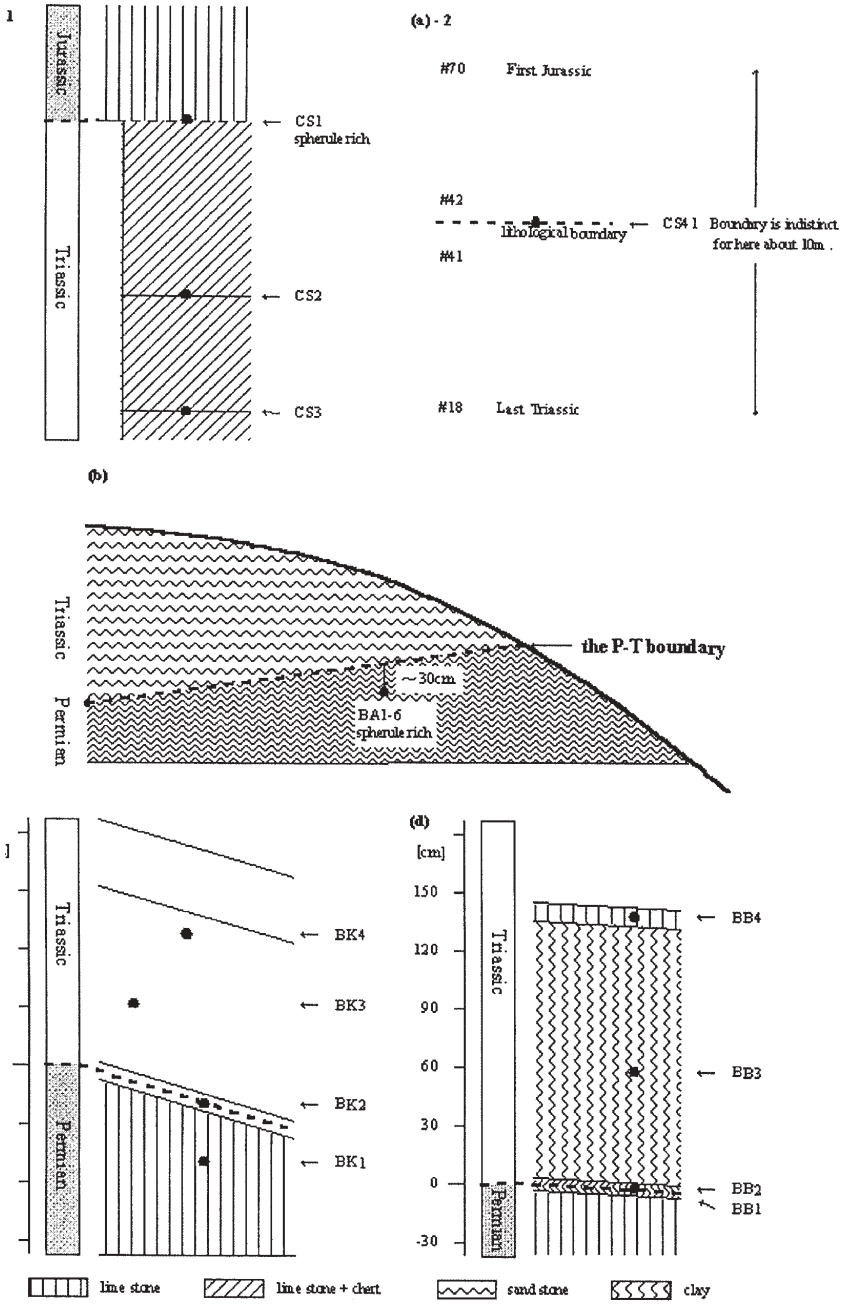

Fig.2. Layers of (a) CS, (b) BA, (c) BK and (d) BB section. Sampling points are indicated by solid circles

cosmogenic ^{3}He production is a very near surface process (~a few meters from the surface) and that the amount of cosmogenic ^{3}He from the surface to some depth should follow some trend which can be mode led by the attenuation of cosmic rays in the sediments, the latitude, altitude, sedimentation and erosion rates and chemistry of the host sediment, and so on. An important point here is that we can expect that the depth profile of cosmogenic ^{3}He and that delivered by the extraterrestrial matters are quite different; the former would be gradual and the latter should be more pulse-like; so that these two processes can easily be distinguished from each other. The effect of the nucleogenic ^{3}He should primary be a function of lithium contents which we do not analyse here; but judging from the relatively uniform major elemental composition determined by XRF, we can suspect that their mineral composition is more or less similar; in such a case, we also do not expect to see a pulse-like peak in ^{3}He concentration, if we plot data in a ^{3}He versus distance diagram.

With the above reasoning, we plot the ^{3}He concentrations of T-J and P-T samples vs. the distance from their respective boundary in figure 5. The concentration of ^{3}He in the T-J samples are less variable with a factor of about three compared with that of ^{4}He showing a nearly one order of variation. The samples just at the T-J boundary are the lowest and do not show a pulse-like peak in ^{3}He concentrations as expected by the extraterrestrial contribution. So the variation in ^{3}He in those samples is not clear. In contrast, the P-T boundary samples BB and BK series, collected off the boundary samples are clearly having very low ^{3}He concentration of below 10^{-14} cm^{3}STP/g, whereas two samples (BK and BB) have an about 4 to 5 times higher ^{3}He concentration than the upper and lower sections. This is clearly a pulse-like peak thus might be suggesting an input of ^{3}He form some exotic source at the time of the deposition of the P-T boundary layer. Of course, it is still premature to conclude that this is related to some impact event and had caused the mass extinction, because we still need to consider many factors which might affect the ^{3}He concentration of sedimentary rocks. For example, we need to evaluate the Li contents to see if there are some Li-rich phases contained exclusively in the at-boundary

Sample		Weight [g]	[^{3}He] x10^{-13}		[^{4}He] x10^{-7}		^{3}He/^{4}He x10^{-7}	
T-J section samples								
CS1		0.09776		0.674		2.371		2.84
			±	0.150	±	0.056	±	0.63
CS2		0.12514		1.175		2.675		4.39
			±	0.249	±	0.063	±	0.92
CS3		0.12331		1.754		8.454		2.07
			±	0.395	±	0.199	±	0.46
CS41		0.28759		0.408		0.703		5.81
			±	0.115	±	0.012	±	1.63
P-T section samples								
BA1-6		0.07113		3.026		328.252		0.09
			±	0.820	±	6.016	±	0.02
BK1		0.08588		0.033		0.091		3.59
			±	0.016	±	0.002	±	1.70
BK2		0.11847		0.552		2.671		2.07
			±	0.135	±	0.049	±	0.50
BK3		0.11258		0.105		1.182		0.89
			±	0.032	±	0.022	±	0.27
BK4		0.11308		0.033		0.166		1.99
			±	0.010	±	0.003	±	0.61
BB1		0.10536		0.422		0.793		5.32
			±	0.113	±	0.019	±	1.42
BB2	run1	0.08596		0.076		0.609		1.24
			±	0.023	±	0.011	±	0.38
	run2	0.09758		0.038		0.752		0.50
			±	0.017	±	0.018	±	0.22
BB3		0.10016		0.053		0.367		1.44
			±	0.018	±	0.009	±	0.50
BB4		0.09645		0.221		0.561		3.94
			±	0.055	±	0.013	±	0.97
Air				—		—		13.99

[^{m}X] is the concentration of element X with mass m.
The unit of concentration is shown by cm^{3}STPg^{-1}.
All samples are measured at 1600°C.

Table 2
ELEMENTAL CONCENTRATIONS AND ISOTOPIC RATIOS OF He

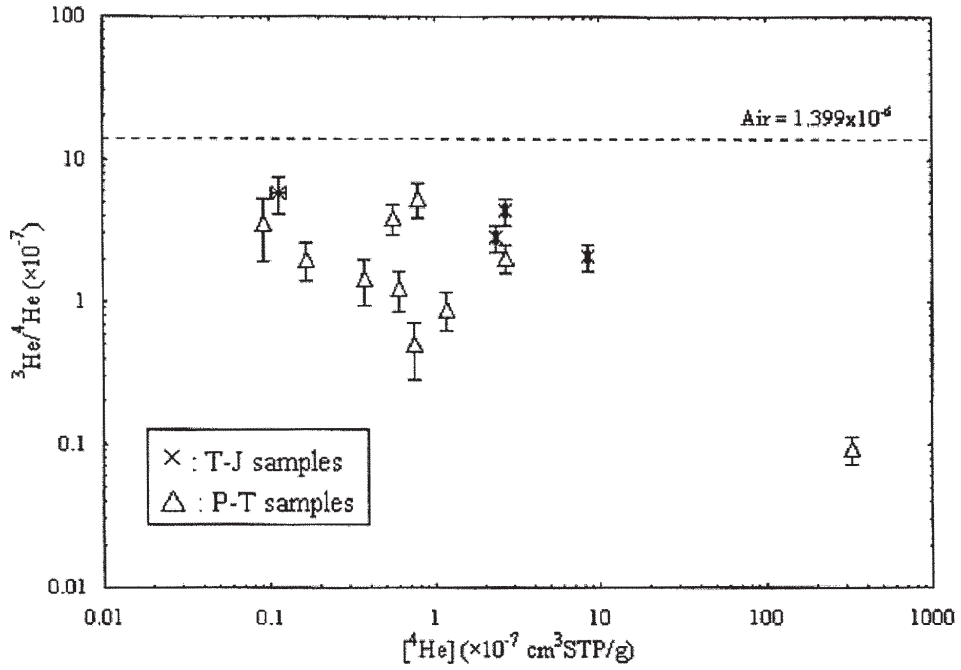

Fig.3. ^{3}He/^{4}He ratios versus ^{4}He concentrations. ^{3}He concentrations in sediments are plotted against ^{4}He concentrations.

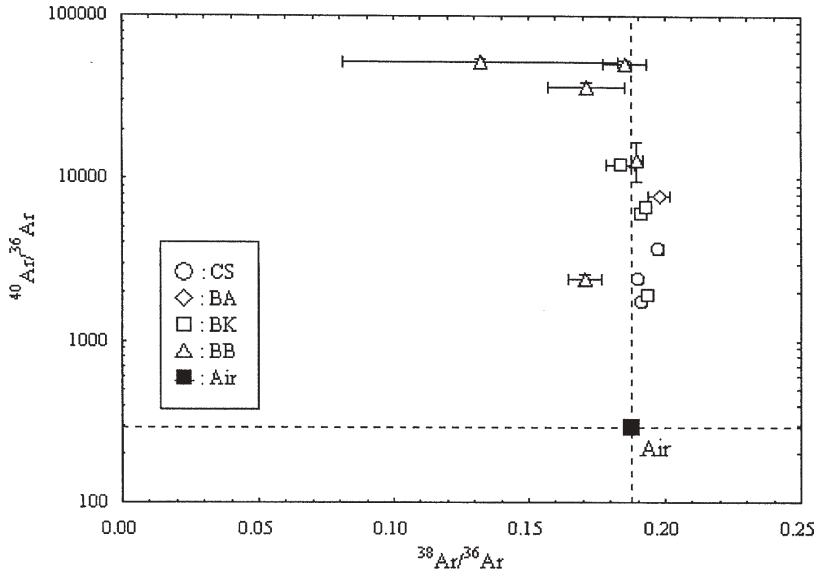

Fig.4. A three-isotope diagram for argon. Each symbol indicates hollow circles for CS1 to CS3, a hollow diamond for BA1-6, hollow triangles for BB1 to BB4, and hollow squares for BK1 to BK4. A large solid square indicates the atmospheric value

Table 3

ELEMENTAL CONCENTRATIONS AND ISOTOPIC RATIOS OF Ar

Sample	Weight [g]	$[^{36}Ar]$ x10^{-9}	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$
T-J section samples				
CS1	0.09776	1.657	0.192	1755
		± 0.178	± 0.001	± 99
CS2	0.12514	1.053	0.197	3675
		± 0.120	± 0.002	± 253
CS3	0.12331	8.047	0.190	2399
		± 0.829	± 0.001	± 114
CS41	0.28759	0.385	——	8213
		± 0.018	——	± 150
P-T section samples				
BA1-6	0.07113	2.339	0.198	7755
		± 0.135	± 0.004	± 219
BK1	0.08588	0.457	0.194	1891
		± 0.026	± 0.002	± 50
BK2	0.11847	1.157	0.191	6075
		± 0.065	± 0.002	± 174
BK3	0.11258	0.158	0.184	12119
		± 0.009	± 0.005	± 338
BK4	0.11308	0.098	0.193	6603
		± 0.005	± 0.002	± 180
BB1	0.10536	0.543	0.190	13191
		± 0.153	± 0.002	± 3520
BB2 run1	0.08596	0.023	0.171	36406
		± 0.002	± 0.014	± 2339
run2	0.09758	0.654	0.171	2398
		± 0.077	± 0.006	± 186
BB3	0.10016	0.017	0.132	51543
		± 0.002	± 0.051	± 2837
BB4	0.09645	0.025	0.185	50457
		± 0.003	± 0.008	± 3218
Air		——	0.188	296

$[^{36}Ar]$ is the concentration of ^{36}Ar.

The unit of concentration is shown by cm^3STPg^{-1}.

All samples are measured at 1600°C.

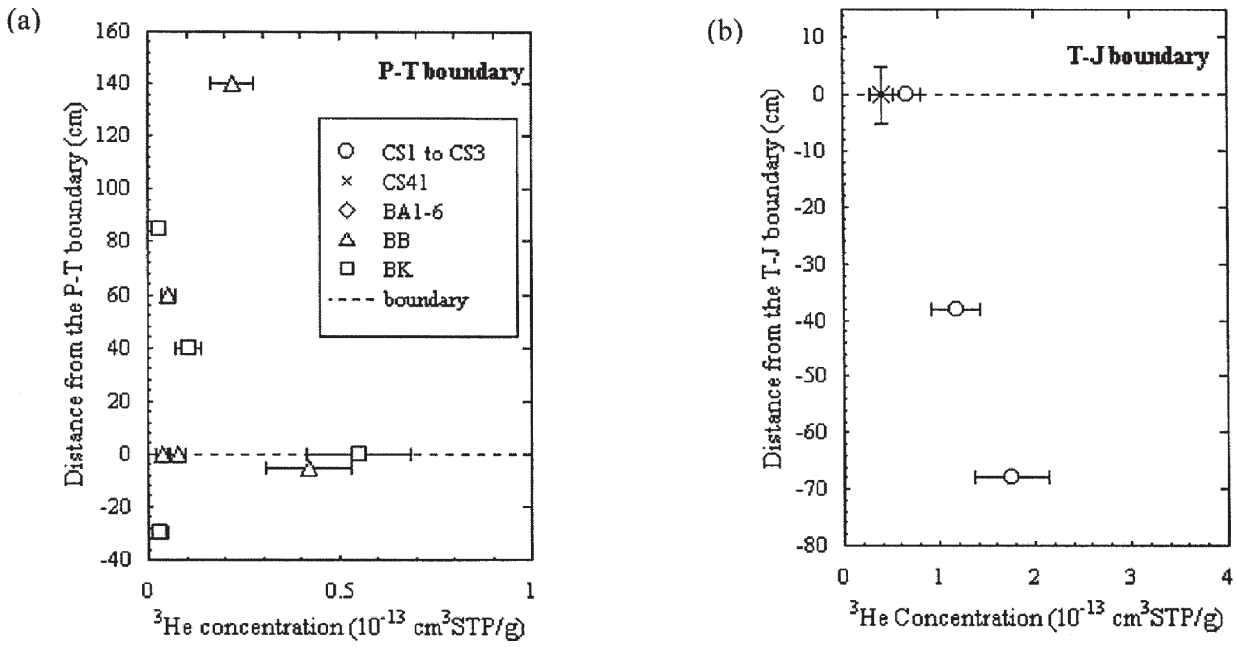

Fig.5. ^{3}He concentrations for the P-T (a) and T-J (b) boundaries. Symbols are the same as in figure 4, and a times sign for CS41. The P-T and T-J boundaries is drawn by the horizontally dotted lines. Sample BA1-6 was not plotted because this sample is a sand stone and its original location is not clear

samples. In spite of the above uncertainties, the present results demonstrate the possibility of detecting some unexpected input of ^{3}He on the P-T boundary which should be of geological importance.

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