Iridium concentration and noble gas composition of Cretaceous–Tertiary boundary clay from Stevns Klint, Denmark

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The Cretaceous–Tertiary (K–T) boundary about 65 million years ago records a mass extinction event caused by a bolide impact. K–T boundary clay collected from Stevns Klint, Denmark was investigated in this work. Iridium concentrations of eight clays across the K–T boundary were determined using a multiple gamma-ray analysis system after neutron activation. Anomalously high Ir concentrations were detected in five marl samples, with the highest concentration being 29.9 ppb. Four samples were analyzed for all noble gases. No extraterrestrial Ar, Kr, and Xe were discovered in any of the samples, although most of the ³He which was detected was extraterrestrial. Solar-like Ne was observed only in the sample SK4, which had an Ir concentration of 14.3 ppb, indicating the presence of micrometeorites. The solar-like Ne clearly did not originate from an asteroid/comet associated with the bolide impact, as that asteroid is thought to have been extremely large. Also, because there was no sign of a high accretion rate of micrometeorites at the boundary it could not be ascertained whether the solar-like Ne was related to a catastrophic event that led to the extinction of the dinosaurs.

Keywords: K–T boundary, iridium, noble gas

INTRODUCTION

It is well known that the concentration of Ir in Cretaceous–Tertiary (K–T) boundary clay is anomalously high, over 30 ppb (Alvarez *et al.*, 1980; Kyte *et al.*, 1980; Kastner *et al.*, 1984). The Ir-anomaly clearly indicates that a bolide impact occurred about 65 million years ago, corresponding to the Chicxulub crater buried beneath the Yucatán Peninsula in Mexico (e.g., Sharpton *et al.*, 1992).

Although noble gas is one of the most sensitive indicators for extraterrestrial material, no extraterrestrial noble gases associated with a bolide impact have been detected in the K–T boundary layer (Eugster *et al.*, 1985; Wolbach *et al.*, 1985; Lewis and Wolbach, 1986; Amari *et al.*, 1988; Takaoka and Miura, 1989). A study by Eugster *et al.* (1985) mainly attempted to find if there was any enrichment of extraterrestrial He in residue treated with HCl and HF. Although they did discover excessive amounts of ³He in some Stevns Klint residue, they attributed it to the outgassing of primordial ³He from the man-

tle of the earth or ⁶Li(*n*, $\alpha\beta$)³He reactions. Lewis and Wolbach (1986) attempted to detect Carbonaceous Chondrite Fission (CCF)-Xe in samples from Stevns Klint and Woodside Creek in New Zealand. Excess fission ¹³⁶Xe was discovered in all the samples after being treated with acid, but most or all of that excess was considered to have resulted from the *n*-induced fission of U. Amari *et al.* (1988) measured the ³He/⁴He ratios of clay from Hokkaido in Japan. However, they could only determine the upper limit of the ³He/⁴He ratio ($<6.2 \times 10^{-6}$), which is not a positive sign of it being extraterrestrial He.

Takaoka and Miura (1989) also measured K–T boundary clay from Stevns Klint and discovered spallogenic He and Ne in a fraction treated with HCl/HF. However, although this is a result positively indicating the presence of extraterrestrial noble gases, it is not demonstrative proof, because spallogenic He and Ne have also been reported in summit lava on Maui (Marti and Craig, 1987). In addition, the concentration of spallogenic He and Ne from a massive object that fell to the earth 65 million years ago (10 ± 4 km in diameter, Alvarez *et al.*, 1980) would be very low.

The lack of extraterrestrial noble gases associated with a bolide impact in the K–T boundary can be explained in

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Table 1. Ir concentration of fish clay

Sample	Weight (mg)	Detection time (sec)	Ir		Noble gas measurement	Color
			ppb	error (%)		
SK1a	62.79	6157	24.7	2.0	√	gray
SK1b	59.23	6545	5.3	4.6	√	light gray
SK2	74.85	4594	27.8	2.4		brown
SK3	62.66	52301	2.2	2.5	√	light gray
SK4	76.70	5386	14.3	2.6	√	gray
SK5	80.93	4931	22.5	2.1		gray
SK6	60.02	5237	4.9	5.1		light gray
SK7	62.50	6170	29.9	2.2		brown
JP1*	74.29	53840	3.0	2.2		

*Geochemical reference sample (Horoman peridotite).

four ways. The first is that primordial noble gas components trapped in a huge meteorite were completely degassed during projection so that no extraterrestrial noble gases remained in the K–T boundary clay. The second is that extraterrestrial noble gases were left there but their concentrations are very low. The third is that the noble gases were lost in the acid treatment. The fourth is that the K–T mass extinction and Ir anomaly have no extraterrestrial cause.

Even if one of these hypotheses is correct, previous studies clearly show that the concentration of extraterrestrial noble gas is low or that carrier phases of noble gases are easily decomposed by acids. The latter finding contradicts the already-known property of chondrites that the trapped primordial noble gas component of chondrites is concentrated in an acid-resistant phase (e.g., Lewis *et al.*, 1975). However, the type of the impact asteroid cannot be completely identified, and the influence of diagenesis of the phase is not understood well.

In our study, the noble gas composition of K–T boundary clays without acid treatment was determined by a highly refined noble gas analytical system, and iridium concentrations of the clays were determined using a multiple gamma-ray analysis system.

SAMPLE

The K–T boundary clay tested in the present study was collected by Nagao K. from Stevns Klint in Denmark in 1992. The specimens were removed from a thin layer of marl, which is known as fish clay. Danish fish clay was subdivided into 4 beds from bed II at the bottom to bed V at the top (Christensen *et al.*, 1973). Under bed II was Maastrichtian white chalk (bed I) and over bed V was Cerithium limestone (bed VI). The samples used in this report were taken from beds II, III, or IV. Bed III was a dark brown color due to weathering of the pyrite con-

cretion. The samples were stored at room temperature and were not dried. The samples are listed in Table 1. Four of eight samples were subjected to noble gas analysis.

EXPERIMENTAL PROCEDURES

Noble gas measurement

The samples were not chemically or physically separated to determine their bulk noble gas composition. The samples were preheated at 150°C for a day in a high vacuum to remove any contaminating atmospheric gases adsorbed to their surfaces. Noble gases were extracted by heating in a tantalum oven, in which the samples were pyrolysed at 900 to 1800°C. All the temperature steps were held for 15 minutes. The extracted gases were then purified using three Ti–Zr getters (getters 1, 2, and 3), and Ar, Kr, and Xe were trapped in a liquid-nitrogen-cooled charcoal trap. Since sedimentary material generally has a large variety of volatile species which can cause problems in the purification process, the released gas was purified for 30 minutes using getter 1. Ne was trapped in a cryogenically cooled trap at 15 K, He was introduced into the mass spectrometer, and the isotopic composition was then analyzed. Ne was released at 45 K from the cryogenically cooled trap and measured using the spectrometer. After Ar, Kr, and Xe were released from the charcoal trap, the Kr and Xe were captured in the cryogenic trap at 100 K and the Ar was then measured. Kr and Xe were released at 135 K and 200 K, respectively, from the trap and measured. The noble gas isotopes were analyzed using a highly sensitive mass spectrometer (modified VG-5400/MS-III). A Daly collector was used to measure the light noble gases (He, Ne and Ar) while the Kr and Xe isotopes were measured using a secondary electron multiplier with an ion counting system. The sensitivities to all the noble gases and mass discrimination effects were calibrated by measuring atmospheric noble

Table 2. Concentration and isotopic ratio of helium and neon

Sample	Weight (g)	^4He (10^{-9} cm ³ STP/g)	^3He (10^{-15} cm ³ STP/g)	$^3\text{He}/^4\text{He}$ (10^{-6})	^{20}Ne (10^{-12} cm ³ STP/g)	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^4\text{He}/^{20}\text{Ne}$
SK1a 1800°C	0.2217	402	308	0.77 ± 0.07	707	9.32 ± 0.22	0.036 ± 0.004	568
SK1b 900°C	0.3789	275	332	1.21 ± 0.20	1296	8.96 ± 0.05	0.035 ± 0.002	212
SK1b 1800°C	0.3789	7	12	1.73 ± 0.57	32	10.2 ± 0.6	0.039 ± 0.011	222
Total	0.3789	282	345	1.22 ± 0.22	1328	8.99 ± 0.11	0.036 ± 0.003	212
SK3 600°C	0.3155	24	25	1.06 ± 0.25	1599	9.29 ± 0.17	0.030 ± 0.004	15
SK3 900°C	0.3155	108	54	0.50 ± 0.10	378	9.19 ± 0.22	0.032 ± 0.003	286
SK3 1200°C	0.3155	7	7	0.99 ± 0.85	8	11.2 ± 1.5	0.052 ± 0.020	811
SK3 1500°C	0.3155	n.d.	n.d.	n.d.	13	9.13 ± 1.38	0.026 ± 0.016	n.d.
SK3 1800°C	0.3155	n.d.	n.d.	n.d.	24	9.86 ± 0.76	0.030 ± 0.011	n.d.
Total	0.3155	139	86	0.62 ± 0.28	2023	9.28 ± 0.25	0.031 ± 0.004	69
SK4 1000°C	0.5542	11.7	7.1	0.61 ± 0.26	4.18	11.6 ± 1.6	0.091 ± 0.021	2805
SK4 1100°C	0.5542	5.2	7.2	1.38 ± 0.52	7.89	12.5 ± 0.8	0.095 ± 0.009	660
SK4 1200°C	0.5542	0.51	n.d.	n.d.	6.91	12.7 ± 1.5	0.039 ± 0.010	73
SK4 1300°C	0.5542	0.33	n.d.	n.d.	1.94	15.3 ± 2.9	0.145 ± 0.043	171
SK4 1400°C	0.5542	0.77	n.d.	n.d.	1.39	9.6 ± 4.5	0.024 ± 0.042	550
SK4 1600°C	0.5542	0.03	n.d.	n.d.	5.97	9.6 ± 2.4	0.023 ± 0.019	n.d.
SK4 1800°C	0.5542	n.d.	n.d.	n.d.	3.40	9.4 ± 3.9	0.030 ± 0.034	n.d.
Total	0.5542	18.6	>14.3	0.85 ± 0.411	32	11.6 ± 2.3	0.062 ± 0.022	586

Calculated from 1000°C and 1100°C fractions.

gases and a standard helium gas with $^3\text{He}/^4\text{He} = 1.71 \times 10^{-4}$ prepared by mixing pure ^3He and ^4He gases at our laboratory. The mass interference of $^{40}\text{Ar}^{++}$ and CO_2^{++} in the neon analysis was corrected using experimentally determined $^{40}\text{Ar}^{++}/^{40}\text{Ar}^+$ and $\text{CO}_2^{++}/\text{CO}_2^+$ ratios (Osawa, 2004). For the Ne analysis, the argon and carbon dioxide were removed using a liquid-nitrogen-cooled trap beside a source of ions. The background was determined by heating an empty Mo crucible. The background levels of ^4He , ^{20}Ne , ^{40}Ar , ^{84}Kr , and ^{132}Xe at 1800°C were 9.89×10^{-10} cm³STP, 2.91×10^{-12} cm³STP, 7.21×10^{-10} cm³STP, 5.46×10^{-14} cm³STP, and 1.19×10^{-15} cm³STP, respectively.

Neutron activation analysis

Iridium concentration can be determined using Instrumental Neutron Activation Analysis (INAA) with the multiple gamma-ray detection method. The nuclide quantification method was developed by Oshima *et al.* (Toh *et al.*, 2001; Hatsukawa *et al.*, 2002; Oshima *et al.*, 2002, 2008) and has been successfully applied in a variety of fields. The iridium in the geological samples was determined using the multi-parameter coincidence method with no chemical separation after neutron irradiation. Fifty to one hundred mg of ground homogenized fish clay sediment samples were sealed in pure quartz vials and then irradiated for 48 hours in the JRR-3 reactor at JAEA with a neutron flux of 9.6×10^{13} ncm⁻²s⁻¹. 100 ng standard

iridium samples made from diluted Ir standard solution (ACROS Organic Co.) were also prepared, sealed in quartz vials, and then irradiated together with the sediment samples. After irradiation, the samples were cooled for about four weeks. The gamma ray decay was measured using GEMINI-II, an array of 16 high purity Ge detectors, with a typical measurement taking about a day. The γ - γ coincidence peak of 468–316 keV from ^{192}Ir ($T_{1/2} = 73.8$ d) produced by the $^{191}\text{Ir}(n,\gamma)^{192}\text{Ir}$ reaction was used in quantitative analysis. All the samples were measured with a standard ^{133}Ba source to perform dead-time calibration of the detector system. The iridium content of the sediment samples was obtained by comparing the ^{192}Ir intensity of the sediment samples with the standard iridium after decay time corrections.

RESULTS

Ir concentration

The measured Ir concentrations of the 8 samples are listed in Table 1. The one-sigma errors are lower than 6%. Anomalously high concentrations over 10 ppb are detected in 5 of the samples. The highest concentration, 29.9 ppb, is found in SK7, which is consistent with the previously reported values of 31.0 and 36.0 ppb in bed II or III (Kyte *et al.*, 1980). The Ir concentrations of the four samples for which noble gas analysis was carried

Table 3. Concentration and isotopic ratio of heavy noble gases

Sample	Weight (g)	^{40}Ar (10^{-9} cm ³ STP/g)	^{36}Ar (10^{-9} cm ³ STP/g)	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{38}\text{Ar}/^{36}\text{Ar}$	^{84}Kr (10^{-12} cm ³ STP/g)	^{132}Xe (10^{-12} cm ³ STP/g)	$^{36}\text{Ar}/^{132}\text{Xe}$	$^{84}\text{Kr}/^{132}\text{Xe}$
SK1a	0.2217	2,544	3.192	797 ± 9	0.1896 ± 0.0003	296	86	37	3.5
SK1b 900°C	0.3789	99,012	319	310 ± 2	0.1898 ± 0.0017	13,470	1,311	243	10.3
SK1b 1800°C	0.3789	529	0.14	3742 ± 20	0.1909 ± 0.0012	5.3	0.49	291	10.9
Total		99,542	319	312 ± 2	0.1898 ± 0.0017	13,475	1,312	243	10.3
SK3 600°C	0.3155	383	0.289	1322 ± 1	0.1900 ± 0.0011	7.12	0.33	872	21.4
SK3 900°C	0.3155	1,521	4.749	320 ± 1	0.1890 ± 0.0017	41.3	3.65	1300	11.3
SK3 1200°C	0.3155	139	0.046	3017 ± 19	0.1910 ± 0.0019	2.42	0.28	166	8.7
SK3 1500°C	0.3155	11	0.024	471 ± 4	0.1864 ± 0.0022	0.44	0.04	573	10.7
SK3 1800°C	0.3155	10	0.033	296 ± 2	0.1881 ± 0.0023	0.90	0.06	554	14.9
Total		2,064	5.141	401 ± 2	0.1890 ± 0.0017	52.2	4.37	1178	11.9
SK4 1000°C	0.5542	76	0.011	7184 ± 175	0.1920 ± 0.0037	0.55	0.04	286	14.9
SK4 1100°C	0.5542	296	0.032	9163 ± 294	0.1911 ± 0.0017	1.63	0.15	221	11.1
SK4 1200°C	0.5542	197	0.028	7082 ± 179	0.1911 ± 0.0022	2.14	0.20	139	10.7
SK4 1300°C	0.5542	22	0.013	1596 ± 4	0.1926 ± 0.0025	0.19	0.01	966	13.6
SK4 1400°C	0.5542	11	0.010	1091 ± 5	0.1918 ± 0.0029	0.10	0.01	1039	10.2
SK4 1600°C	0.5542	7	0.008	867 ± 11	0.1883 ± 0.0036	0.20	0.02	507	12.5
SK4 1800°C	0.5542	3	0.009	341 ± 2	0.1893 ± 0.0039	0.30	0.02	342	12.0
Total		612	0.111	5509 ± 190	0.1911 ± 0.0026	5.11	0.45	248	11.4

out varied. SK3 and SK1b had the relatively low Ir concentrations of 2.5 and 4.6 ppb, respectively. On the other hand, SK1a and SK4 have anomalously high Ir concentrations of 24.7 and 14.3 ppb, respectively, leading to the conclusion that extraterrestrial material is present.

Noble gas composition

The measured noble gas concentrations and isotopic ratios of the four clay samples are summarized in Tables 2 and 3. The error is one sigma.

Helium ^3He is a very sensitive tracer of micrometeorites in sediments and is used to estimate the influx of micrometeorites onto the Earth (e.g., Farley, 1995; Mukhopadhyay *et al.*, 2001). The extraterrestrial fraction of ^3He in the sediments can be calculated from $^3\text{He}/^4\text{He}$ ratio which is modeled as a simple two-component mixture of crustal and extraterrestrial He (Takayanagi and Ozima, 1987; Farley, 1995). $^4\text{He}/^{20}\text{Ne}$ ratios of the clay samples are more than 200 times the atmospheric ratio, 0.32 (Table 2), proving that the contribution of atmospheric ^3He is negligible. Assuming a $^3\text{He}/^4\text{He}$ ratio of 1.99×10^{-8} for clay (Andrews, 1985), the calculated extraterrestrial ^3He accounts for at least 96% of the total ^3He .

It is notable that there is no correlation between Ir and ^3He concentration. The highest ^3He concentration of 3.45×10^{-13} cm³STP/g is found in SK1b, in which a low concentration of Ir (5.3 ppb) was detected. On the other hand, the lowest ^3He concentration of $>1.43 \times 10^{-14}$ cm³STP/g is observed in SK1b, which has a high Ir concentration of 14.3 ppb. SK1a has the highest Ir concen-

tration (24.7 ppb) and high ^3He concentration (3.08×10^{-13} cm³STP/g). The discrepancy between Ir and ^3He concentration can be explained by positing that ^3He concentration is affected by two factors: nonuniformity of the small number of micrometeorites stored in the clays and high variation of the accumulation rate. Since there is no correlation between Ir and ^3He concentration, it is clear that most of the extraterrestrial ^3He in the K–T boundary clays is not due to a bolide hitting the earth, and originates from micrometeorites accreted on the Earth.

Takaoka and Miura (1989) reported a definite excess of ^3He in a sample of Stevns Klint clay treated with HCl/HF. They found a $^3\text{He}/^4\text{He}$ ratio of $97 \pm 3 \times 10^{-6}$, which is 69 times the atmospheric value. However, no such high isotopic ratios are found in our samples, which is presumably because there was no separation of the samples. **Neon** The Ne isotopic compositions are plotted in Fig. 1. The Ne released from SK1a, SK1b and SK3 is predominantly atmospheric Ne, their total Ne isotopic compositions corresponding to the results of Takaoka and Miura (1989), in which $^{20}\text{Ne}/^{22}\text{Ne} = 9.43 \pm 0.08$ and $^{21}\text{Ne}/^{22}\text{Ne} = 0.0385 \pm 0.0065$. However, the Ne concentration of SK4 is much lower than the other samples and its isotopic composition is exceptional. Both the $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios of SK4 are clearly higher than those of the atmosphere, revealing the presence of a non-atmospheric source.

The high ratio of $^{20}\text{Ne}/^{22}\text{Ne}$ can be explained by the contribution of the solar wind or mantle, but it is not easy to explain how mantle Ne can exist in marl. Micrometeorites are, therefore, a more plausible source

Fig. 1. Three isotope plot of Ne for SK4 (a) and others (b). The data from all temperature fractions is given. Solar wind (SW)-Ne after Benkert *et al.* (1993) and Air-Ne after Eberhardt *et al.* (1965). Errors are one sigma. The numbers shown in the upper diagram give the temperature in centigrade. The shaded area indicates the range of micrometeorites (e.g., Osawa *et al.*, 2003). In the lower diagram Takaoka and Miura (1989) give the data from SK2-4R, an HCl/HF treated residue.

of the solar-like Ne because micrometeorites retain large amounts of solar noble gases (e.g., Osawa and Nagao, 2002; Osawa *et al.*, 2003) and it is known that solar-derived Ne gets concentrated in deep-sea sediment (Matsuda *et al.*, 1990). The high ratio of $^{21}\text{Ne}/^{22}\text{Ne}$ in SK4 is probably due to nucleogenic ^{21}Ne produced in the $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ reaction, because cosmogenic ^{21}Ne is scarce in micrometeorites (e.g., Osawa and Nagao, 2002). Judging from the overall composition of the Ne in the sample

Fig. 2. Three isotope plot of Ar for all samples. Errors are one sigma. Q-Ar after Busemann *et al.* (2000) and Air-Ar after Nier (1950).

($^{20}\text{Ne}/^{22}\text{Ne} = 11.6$, $^{21}\text{Ne}/^{22}\text{Ne} = 0.062$) the contribution of non-atmospheric Ne is high. This isotopic composition is also due to the low concentration of total Ne, only $3.2 \times 10^{-11} \text{ cm}^3\text{STP/g}$.

The isotopic composition of the Ne in SK1a is different from SK4, with no sign of solar-derived Ne, although the clay did have the highest Ir concentration of all the samples, thus revealing the presence of extraterrestrial material. The Ne trapped in SK1a is almost all terrestrial. Assuming that all ^3He is derived from micrometeorites and that the average $^3\text{He}/^{20}\text{Ne}$ ratio of micrometeorites is 0.0085 (Nakamura and Takaoka, 2000), the contribution of solar-Ne can be roughly estimated from the concentrations of ^3He . The contributions of micrometeorite-derived ^{20}Ne in SK1a, SK1b, SK3 and SK4 are 5.1%, 3.1%, 0.5% and >5.3%, respectively. The low value of >5.3% in SK4 might indicate a preferential loss of ^3He , although the mechanism is not clear.

Heavy noble gases Ar isotopic composition is the most sensitive indicator for extraterrestrial samples that have been heavily contaminated or degassed through heating or alteration. There are three reasons why Ar is a sensitive indicator for extraterrestrial material: 1) The sensitivity of the mass spectrometer to Ar is higher than to He or Ne. 2) Mass interferences of ^{36}Ar , ^{38}Ar , ^{40}Ar are not serious in a mass spectrometer with mass resolution of 600. 3) The shift of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is very large, because most ^{40}Ar is produced from the electron-capture radioactive decay of ^{40}K . Osawa and Nagao (2003) revealed that about 40% of totally melted spherules contain extraterrestrial Ar because the Ar is well preserved compared to He and Ne.

Fig. 3. Heavy noble gas elemental compositions for all fractions. Eugster *et al.* (1985) give the total amount of noble gases released from Stevns Klint 2 residue (run2) that had been treated with HCl/HF. Heavily fractionated terrestrial atmosphere is found in SK1a. Saturated noble gases in sea water at 25 °C as calculated by Ozima and Podosek (2002).

Since ^{40}Ar in primordial Ar in the solar system is scarce, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio can provide important information on extraterrestrial materials when the radiogenic ^{40}Ar and atmospheric contamination are not exceptionally large. A three isotope plot of the K–T boundary clay is given in Fig. 2. No sample has a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio lower than that of the terrestrial atmosphere, 296. SK1a and SK4, with their high Ir concentrations, have high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, reflecting the presence of radiogenic ^{40}Ar produced from *in situ* radioactive decay of ^{40}K . The Ar isotopic ratios of SK1b and SK3 are near that of the atmosphere. $^{38}\text{Ar}/^{36}\text{Ar}$ ratios higher than that of the atmosphere, 0.188, are found in all the samples, presumably indicating the presence of nucleogenic ^{38}Ar originating from the $^{35}\text{Cl}(\alpha, p)^{38}\text{Ar}$ reaction. As in the case of Eugster *et al.* (1985), there is no sign of extraterrestrial Ar isotopes in our samples.

The elemental compositions of Ar, Kr, and Xe are given in Fig. 3. All the samples have $^{84}\text{Kr}/^{132}\text{Xe}$ and $^{36}\text{Ar}/^{132}\text{Xe}$ ratios lower than that of the terrestrial atmosphere, SK1a in particular being near the region of chondrite matrices. However, elemental compositions do not demonstrate the presence of extraterrestrial noble gases because adsorbed gases get heavily fractionated (Scherer *et al.*, 1994). Eugster *et al.* (1985) also reported low $^{84}\text{Kr}/^{132}\text{Xe}$ and $^{36}\text{Ar}/^{132}\text{Xe}$ ratios. SK1b contains very large amounts of Ar, Kr, and Xe compared to the other samples (Table 3) and its $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 312 ± 2 is close to that

of terrestrial atmosphere, indicating that the high concentrations of heavy noble gases are mainly due to adsorbed air. However, the elemental composition of the clay is significantly fractionated ($^{36}\text{Ar}/^{132}\text{Xe} = 243$, $^{84}\text{Kr}/^{132}\text{Xe} = 10.3$). The cause of the exceptionally high concentrations of heavy noble gases in SK1b may be large surface area due to the grain size.

The Xe isotopic compositions, which are not specifically analyzed here, are closer to the terrestrial atmosphere than any other extraterrestrial source.

DISCUSSION

There is no evidence of extraterrestrial Ar, Kr, or Xe. However, the Ne in SK4 clearly indicates the presence of solar-derived Ne, which presumably originated in micrometeorites. In fact, when the nucleogenic (or cosmogenic) Ne is subtracted from the overall Ne, the corrected Ne composition corresponds to that of micrometeorites (Fig. 1).

It is, however, very difficult to accept that a bolide hitting the earth would include a lot of solar-derived Ne, because solar winds can only penetrate several hundred angstroms into the surface of rock (Benkert *et al.*, 1993). Further, since the diameter of the asteroid has been estimated to be 10 ± 4 kilometers (Alvarez *et al.*, 1980) the amount of solar-Ne is negligible. The solar-derived Ne therefore seems to be unrelated to the asteroid itself.

If the source of the solar-derived Ne is micrometeorites, can it then be said that a flux of extraterrestrial dust rose at the K–T boundary? Mukhopadhyay *et al.* (2001) measured the He concentration in marine carbonates throughout a time span of 63.9 to 65.4 million years ago and concluded that the bolide associated with the K–T extinction event was not accompanied by enhanced solar system dustiness, due to the near-constant ^3He accretion rate across the boundary. The detected solar-like Ne might be merely due to low interference of atmospheric Ne.

The $^3\text{He}/^{20}\text{Ne}$ ratio of SK4, 0.00045, is significantly lower than that of average micrometeorites, 0.0085 (Nakamura and Takaoka, 2000), and the noble gas concentrations of SK4 are much lower than those of other samples. The result may reflect noble gas depletion by heating. In a stepwise heating experiment performed on micrometeorite-bearing particles separated from Antarctic ice, about 87% of He was extracted at 700 °C but about 71% of Ne still remained (Nakamura and Takaoka, 2000). Indeed, severely heated extraterrestrial particles, such as cosmic spherules, have a low He/Ne ratio (Osawa and Nagao, 2003). In the age when SK4 cumulated, severely heated extraterrestrial particles, e.g., particles with very fast relative speed to the Earth, might have been predominant, and the event might be linked with some kind of

astronomical phenomenon.

Our results also show that noble gases trapped in the K–T extraterrestrial projectile had been mostly depleted. If the Ir concentration of the projectile is assumed to have been 470 ppb, which is a typical concentration in CI chondrite and reflects the solar abundance, the extraterrestrial material in SK1a was diluted to 1/19. Further, if the ^{36}Ar concentration of the projectile is assumed to have been $8.0 \times 10^{-7} \text{ cm}^3\text{STP/g}$, which is the average concentration in CI chondrite, the ^{36}Ar concentration in SK1a should be $4.2 \times 10^{-8} \text{ cm}^3\text{STP/g}$, thirteen times higher than the ^{36}Ar concentration in SK1a found in this study. In SK4, only 0.45% of the extraterrestrial ^{36}Ar is estimated to have remained in the clay. This indicates that there was a rise in temperature to over 1000°C , which explains why the noble gases almost completely escaped from the noble gas carriers of the bolide even though the primordial noble gas component trapped in the chondrite was tightly captured.

Although a highly sensitive mass spectrometer was used, no sign of chondritic noble gases was found in this study. Even if the sensitivity of mass spectrometers is greatly improved in the future, it will still be difficult to identify the noble gases associated with the projectile without the analysis of a large amount of the K–T boundary clay.

CONCLUSION

The Ir concentrations of eight K–T boundary samples collected from Stevns Klint were measured, and four of them were subjected to noble gas analysis. Five of the samples had Ir anomalies, with the highest value being 29.9 ppb, which is consistent with previously reported concentrations. As in the case of previous noble gas research conducted on K–T boundary clay, there was no sign of extraterrestrial Ar, Kr, and Xe isotopic and elemental compositions in the Stevns Klint samples. The compositions of these three elements can be explained as being due to the contribution of adsorbed terrestrial atmosphere, radiogenic nuclides, and nucleogenic nuclides. On the other hand, most of the ^3He is extraterrestrial and can be traced to micrometeorites. Solar-like Ne was observed in SK4, in which the relatively high Ir concentration of 14.3 ppb was detected through multiple gamma-ray analysis. The source of the solar-like Ne was presumed to be micrometeorites accreted on the earth, because micrometeorites preserve solar noble gases. That said, though the projectile associated with the K–T extinction was massive, the amount of solar-derived Ne it contained was negligible when compared with the overall amount of Ne. Further, no evidence of a dramatic increase in the accretion rate of extraterrestrial dust was discovered. It is, therefore, still unclear whether the solar-like Ne is re-

lated to the mass extinction event that led to the extinction of so many living things.

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