

NOBLE GASES IN THE K-T BOUNDARY CLAY FROM STEVNS KLINT, DENMARK

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Abstract: Helium and neon isotopes were investigated in two beds of the Cretaceous-Tertiary (K-T) boundary collected at Stevns Klint in Denmark. Observed enrichments in ³He and ²¹Ne relative to atmospheric abundances suggest that the K-T boundary sediment contains spallogenic He and Ne. Although this is a favorable result for the asteroid impact hypothesis, we need more data on noble gas isotopes not only in the K-T boundary sediments but also in sedimentary rocks other than the K-T boundary.

1. Introduction

Many reports (*e.g.*, ALVAREZ, 1986; HALLAM, 1987) on studies of K-T boundary material have been published since ALVAREZ *et al.* (1980) had determined a high Ir concentration in the K-T boundary clay at Gubbio, Italy. These authors proposed that a large asteroid impact caused mass extinctions at the end of the Cretaceous. However, in spite of extensive studies on the K-T boundary material, experimental evidence has not solved the question what happened at the end of the Cretaceous.

Noble gases are sensitive tracers for extraterrestrial matter because they are less abundant in terrestrial material and because they can be detected with high sensitivity by modern mass spectrometry. The large difference in a specific isotopic ratio between terrestrial and meteoritic noble gases enhances the sensitivity to identify the meteoritic gas. The noble gases can be diagnostic for the existence of debris of the impacting asteroid if parts of it never melted.

For acid-etched residues of the K-T boundary clay from Stevns Klint, EUGSTER *et al.* (1985) have reported the terrestrial isotopic compositions of noble gases except He. A ³He/⁴He ratio as high as 24 times the atmospheric ratio has been observed in one sample. These authors have assigned the high He isotopic ratio to mantle He. From Xe isotopic data for acid-etched residues of the K-T boundary clays from Stevns Klint (WOLBACH *et al.*, 1985), and from Stevns Klint and Woodside Creek in New Zealand (LEWIS and WOLBACH, 1986), it has been concluded that the undegassed fraction of meteorite is very small in these K-T boundary clays. AMARI *et al.* (1988) analysed a K-T boundary clay sample from Hokkaido in Japan for He isotopes, but they could find no isotopic enrichment in ³He.

2. Samples and Experimental Procedure

Samples analysed in this work were collected at a cliff near the Højerup Church at Stevns Klint in Denmark. Sample numbering is in accordance with that for beds originally studied by CHRISTENSEN *et al.* (1973). The numbers following hyphens correspond to the bed numbers of CHRISTENSEN *et al.*

According to these authors, bed 3 is composed of reduced, black marl including sulfide minerals, and bed 4 of dark to grey layered marl. Mineralogical and ESR studies of these samples have been reported elsewhere (MIURA *et al.*, 1985). Figure 1 shows a flow chart of sample preparation. Both beds 3 and 4 were analysed for bulk samples. The remaining part of the bed 4 clay, weighing 52 g, was treated with 6N-HCl and concentrated HF at room temperature for two days, in order to remove CaCO₃ and silicates. Contrary to anticipation, there remained a considerable amount (16.4 g) of residue. This can be assigned to incomplete dissolution of fluoride minerals which were produced by reactions between HF and silicates and covered silicate grains to prevent them from further chemical attack by HF. The EPMA images of grains in the residue show layered structures of whitish minerals surrounding silicates in the center. Approximately one-third of the residue, weighing 5.08 g, was used for sample SK2-4R.

The remaining part of the residue was separated further to three density fractions. SK2-4RW is a fraction heavier than 2.25 g/ml. SK2-4RBL and SK2-4RBR are lighter than 2.25 g/ml, and black and brown in color, respectively. SK2-4RBL and SK2-4RBR were separated by difference in sedimentation velocity in a centrifugal tube.

Samples wrapped with Al-foil were mounted in a sample holder of a gas extraction furnace and kept in vacuum for a few days. Concentrations and isotopic ratios of He and Ne were measured by conventional techniques of noble gas mass spectrometry (TAKAOKA, 1976). The system blanks are less than 1×10^{-12} , 1×10^{-9} and

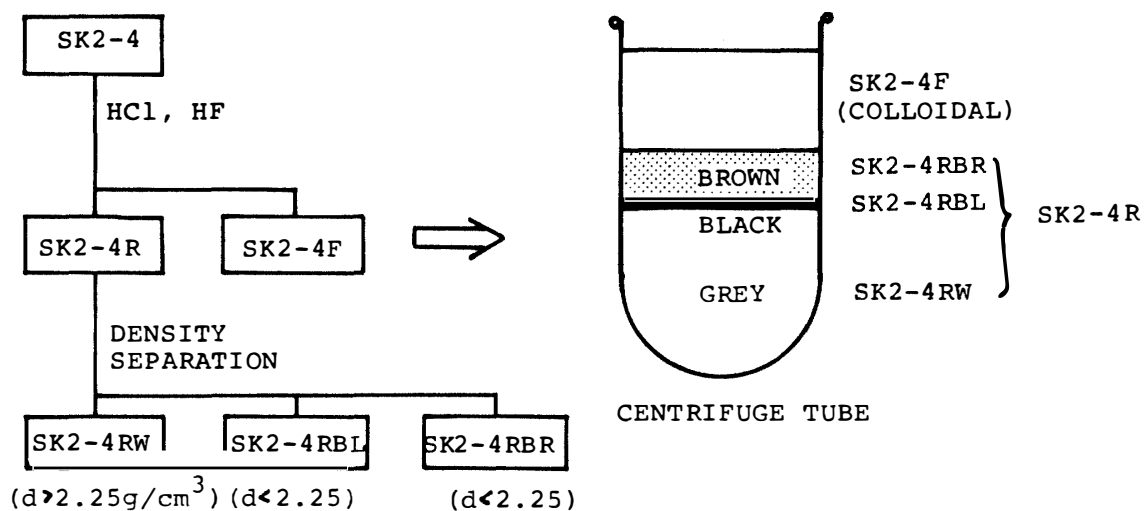


Fig. 1. Flow chart of sample preparation. Approximately one-third of residue SK2-4R including brown, black and grey portions was used for noble gas analysis. The remaining two-thirds of residue SK2-4R was used for density separation.

8×10^{-13} ml for ^3He , ^4He and ^{21}Ne , respectively.

3. Results and Discussion

Table 1 summarizes the data on He isotopes which are corrected for mass discrimination. Blank correction is practically negligible. Errors (2σ) cited are statistical ones including errors for the mass discrimination correction. For SK2-4R, we find a definite excess in ^3He relative to atmospheric He, 69 times the atmospheric $^3\text{He}/^4\text{He}$ ratio. For other samples, we do not find any definite signals at ^3He . Numerical figures given for ^3He are upper limits estimated from the detection limit of the mass spectrometer. It is noted that both ^3He and ^4He concentrations are highest for SK2-4R. This suggests that such anomalous He as found in SK2-4R is not contained uniformly in the K-T clay, but that it resides in particular undegassed grains.

The $^3\text{He}/^4\text{He}$ ratios for meteoritic He are as high as 0.2 for spallogenic He (*e.g.*, OZIMA and PODOSEK, 1983), 4×10^{-4} for solar-type He (GEISS *et al.*, 1972) and 1.4×10^{-4} for planetary-type He (BLACK and PEPIN, 1969). High $^3\text{He}/^4\text{He}$ ratios up to or beyond 1×10^{-4} have been reported in terrestrial diamonds (OZIMA and ZASHU, 1983; HONDA *et al.*, 1987; ZADNIK *et al.*, 1987), deep sea sediments (FUKUMOTO *et al.*, 1986; AMARI and OZIMA, 1988) and lavas (KURZ, 1986; CRAIG and PODERA, 1986). Therefore, the high He isotopic ratio is not sufficient to identify extraterrestrial origin of the investigated material. The high He isotopic ratios, however, are accompanied by high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios for diamonds (OZIMA and ZASHU, 1988; HONDA *et al.*, 1987) and deep-sea sediments (FUKUMOTO *et al.*, 1986; AMARI and OZIMA, 1988). The high He isotopic ratios in lavas have been assigned to cosmogenic ^3He produced by cosmic-ray interactions with lavas at high mountains (KURZ, 1986). The high He isotopic ratio accompanied by spallogenic Ne has been reported in the summit lavas of Maui (MARTI and CRAIG, 1987).

Table 2 shows the Ne isotopic ratios for SK2-4R. The Ne isotopic ratios for

Table 1. Isotopic abundances of He in Stevns Klint clay samples. Atmospheric He is given for comparison.

Sample (Weight)	$^3\text{He}^{\text{a)}$	$^4\text{He}^{\text{a)}$	$^3\text{He}/^4\text{He}$
SK2-3 (bulk) (0.298g)	$<0.008^{\text{b)}$	100	$<80 \times 10^{-6}$
SK2-4 (bulk) (0.470g)	$<0.005^{\text{b)}$	240	$<20 \times 10^{-6}$
SK2-4R (5.08g)	0.029	300	$(97 \pm 3) \times 10^{-6}$
SK2-4RBR (0.137g)	$<0.002^{\text{b)}$	4	$<400 \times 10^{-6}$
SK2-4RBL (0.026g)	$<0.014^{\text{b)}$	70	$<200 \times 10^{-6}$
SK2-4RW (0.177g)	$<0.0003^{\text{b)}$	10	$<30 \times 10^{-6}$
Atmosphere	—	—	1.4×10^{-6}

a) Concentration is given in 10^{-9} ml/g.

b) Upper limits estimated from the detection limit of mass spectrometer.

Table 2. Isotopic abundances of Ne in SK2-4R. Atmospheric, spallogenic and planetary-type Ne are shown for comparison.

Sample	^{20}Ne	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$
SK2-4R	3 ^{a)}	9.43 ± 0.08	0.0385 ± 0.0065
Atmosphere	—	9.80 ± 0.08	0.0290 ± 0.0002
Spallation	—	0.85	0.92
Planetary (Ne-A)	—	8.2	0.024

^{a)} Concentration is given in 10^{-9} ml/g.

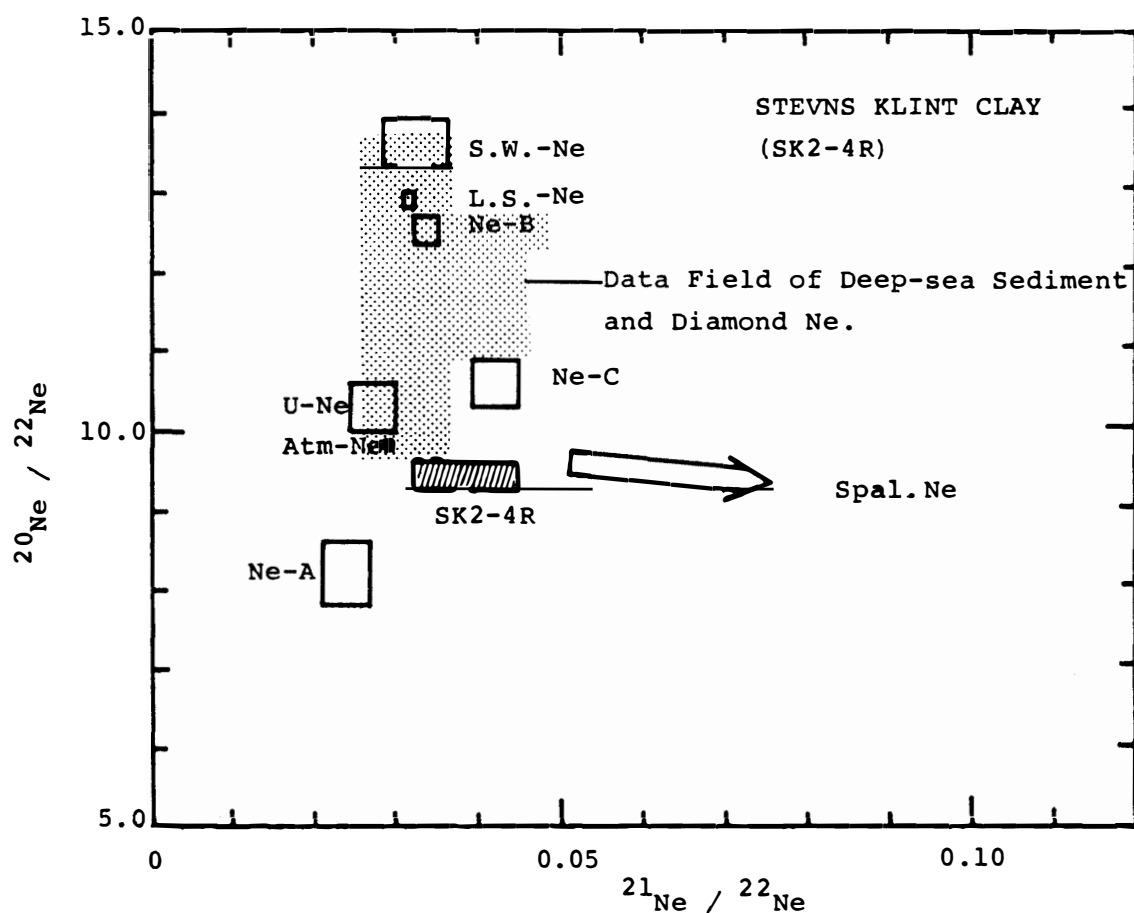


Fig. 2. Three isotope plot diagram of Ne. Ne data for SK2-4R are plotted along a line connecting between atmospheric and spallogenic Ne, which suggests that sample SK2-4R contains spallogenic Ne. Data sources of extraterrestrial Ne are referred to OZIMA and PODOSEK (1983). For U-Ne, OTT *et al.* (1984).

other samples could not be determined precisely because of the small amount of Ne and interferences from $^{40}\text{Ar}^{2+}$ at ^{20}Ne and from doubly-charged CO_2 at ^{22}Ne . Corrections for H_2^{18}O and $^{40}\text{Ar}^{2+}$ at ^{20}Ne are less than 0.3% and 1.3%, respectively, and correction for CO_2^{2+} at ^{22}Ne is 1.3% for SK2-4R. For comparison, atmospheric Ne (EBERHARDT *et al.*, 1965), spallation Ne (OZIMA and PODOSEK, 1983) and Ne-A (BLACK and PEPIN, 1969) are listed.

Figure 2 is a three-isotope plot diagram of Ne isotopes for various components

of Ne found in terrestrial and extraterrestrial matters. The isotopic ratios for SK2-4R fall along a line connecting between atmospheric Ne and spallogenic Ne. Extraterrestrial components of Ne are plotted on an upper left of the diagram except for Ne-A and spallogenic Ne for which $^{20}\text{Ne}/^{22}\text{Ne}$ is lower than the atmospheric ratio. The data field of terrestrial diamonds and deep sea sediments is also above the atmospheric Ne.

The He data for SK2-4R are compatible with those for the terrestrial diamonds, the deep sea sediments, the lavas, and for meteorites, while the Ne data are incompatible with them except for the spallation Ne and planetary Ne. On the assumption that Ne in SK2-4R is a mixture of spallogenic, planetary and atmospheric components, the amounts of spallogenic and planetary Ne can be calculated by the following equations:

$$\begin{aligned} 9.80A + 8.2P + 0.85S &= 9.43M \\ 0.029A + 0.024P + 0.90S &= 0.0385M \\ A + P + S &= M, \end{aligned}$$

where A , P , S and M are the amounts of atmospheric, planetary, spallogenic and measured ^{22}Ne , respectively. Table 3 summarizes the result of decomposition of Ne into three components.

If all ^3He determined in SK2-4R is spallogenic, the ratio of spallogenic ^3He to ^{21}Ne is 8.5 ± 4.6 . This is in the range of the production ratio of spallogenic ^3He to ^{21}Ne in meteorites that is 6 ± 2 (e.g., NISHIZUMI *et al.*, 1980). Spallogenic ^4He amounts to 1.5×10^{-10} ml/g and the remaining part of ^4He (i.e. 3.0×10^{-7} ml/g) can be attributed to atmospheric and/or radiogenic He (EUGSTER *et al.*, 1985) because a Th content of 2.8 ppm has been reported for the Stevns Klint Fish clay (KYTE *et al.*, 1980).

There are four possible sources for the extraterrestrial gases in the investigated sample: the debris of the asteroid impact that occurred at the end of the Cretaceous, the debris of meteorites which impacted through the history of the earth, the cosmic-ray irradiation of surface rocks and an experimental artifact such as a memory effect of the analysing system.

The experimental artifact should be tested by analysing a large sample size of clay. However, we measured more than 1×10^{-10} ml ^3He to determine the isotopic ratio for SK2-4R. Therefore, it is believed that the memory effect is small.

The K-T clay was shielded against the cosmic-ray irradiation because it was marine sediment and layered underground for a long time. Therefore, it is unlikely that spallogenic Ne was produced *in situ* in the sediment. However, spallogenic He and Ne have been reported in the summit lavas of Maui (MARTI and CRAIG, 1987),

Table 3. Decomposition of Ne in SK2-4R into three components.

Component	^{20}Ne	^{21}Ne	^{22}Ne
Atmospheric	2550 ± 110	7.5 ± 0.2	260 ± 32
Spallogenic	3.1 ± 1.7	3.4 ± 1.8	3.7 ± 2.0
Planetary	430 ± 170	1.3 ± 0.5	53 ± 21

Concentration of Ne is given in units of 10^{-12} ml/g.

though the spallogenic ^{21}Ne concentration in the Maui lavas is as low as 1/5 to 1/10 times the present result for SK2-4R.

The SK2-4R contains spallogenic He and Ne. This is a favorable result for the asteroid impact hypothesis (ALVAREZ *et al.*, 1980). However, there are no data on influx of undegassed grains which survived atmospheric abrasion in usual meteorite impacts and on the isotopic compositions of noble gases contained in such grains. To give a conclusion to the question whether the grains bearing these extraterrestrial components came from the debris of the asteroid impact or not, we need more data on noble gases not only in the K-T sediments but also in sediments other than the K-T boundary clays.

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