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Elemental and Sr isotope profiles of the Cretaceous-Tertiary (K-T) boundary layers at Medetli, Gölpazari, northwestern Turkey

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Abstract

Major and trace element concentrations and Sr isotope ratios were determined for the Cretaceous-Tertiary (K-T) transitional layers in Medetli, Gölpazari, northwestern Turkey. Late Maastrichtian gray colored sandstone layer (layer A) is overlain by yellow colored sandstone layer (layer B) with thin goethite-rich layers. Lower Paleocene limestone (layer C) overlies layer B. Fossils are absent in layer B. Major elements such as Al_2O_3, MgO, MnO, Na_2O and K_2O are slightly lower in layer B compared with layer A. Trace elements, such as Ba, Rb and Y, are relatively high in layer A than in layer B, while Sr is clearly rich in layer B. Distinct peaks of Fe, Ni, Co, Cr, As and Sb are found in a goethite-rich layer. The Sr isotope ratios (initial $^{87}Sr/^{86}Sr$ ratios) of samples change from layer A (0.7099-0.7112) to layer B (0.7079-0.7084). This abrupt change of Sr isotope ratios is explained by a drastic increase of precipitation rate of sea water Sr to layer B rather than in layer A, and this change may be related to the K-T event. Association with these results and element concentrations including Ir (Arakawa et al., (2003), the actual K-T boundary is situated probably between the top of layer A and the bottom of layer B. In the Medetli region, the deposition of the top of layer A and probably the layer B are considered to have been formed by the K-T and its successive events.

Introduction

As the Cretaceous-Tertiary (K-T) boundary problem is in still continuing interest in the planet Earth history, many workers have focused their studies into K-T boundary layers in the worlds. The researches and modeling have been done from various points of view in many K-T boundary sites globally (e.g., Alvarez et al., 1980; Borhor et al., 1984; Hildebrand et al., 1991; Blum et al., 1993; Koeberl, 1993; Ebihara and Miura, 1996; Kyte et al., 1996; Smit and Hertgen.;, Smit, 1999;

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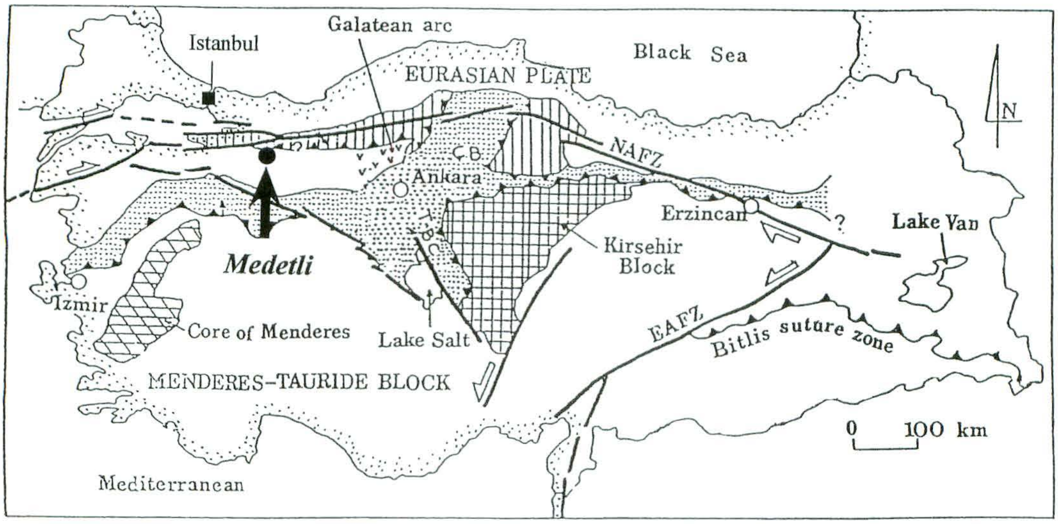

Fig. 1 Sample location (solid circle) of Medetli K-T boundary in Turkey (after Kocygit,1991).

Claeys et al., 2002).

In Turkey, the upper Cretaceous and Palocene sediments are widely developed and the K-T transitional formations are found in several sites. In 1995 and 1996 we have carried out geological field research on the K-T transitional formations of several locations along the Black Sea region (Matsumaru et al., 1996; Matsumaru et al., 1997). In Medetli, Gölpazari (about 120 km southeast from Istanbul) (Fig. 1), a clear section crops out. In our preliminary geochemical report (Arakawa et al., 2003), we presented some element profiles and Ir concentrations for the K-T boundary layers in Medetli, and discovered that Ir concentration is relatively high (0.24 ppb) in the top part of layer A (gray-colored medium grained sandstone). Based upon these results, we proposed a concluding remarks that the actual K-T boundary may be situated between the top of layer A and the bottom of layer B, and both the top of layer A and layer B is assumed to have been formed during the K-T and its successive events.

In this short report, major and trace element profiles of some section in the Medetli are given with the results of our preliminary report. Also we newly present Sr isotope profiles of two sections in the K-T boundary region in Medetli to discuss the relationship with the sea water at that time.

STRATIGRAPHY

In the Medetli region, upper Cretaceous (Maastrichtian) sandstone of the Tarakli Formation is overlaid by the lower Paleocene limestone of the Selvipinari Formation (Dizer and Meriç 1983). The detailed cross sections and sample locations are indicated in Fig. 2. Layers A and B correspond to the Tarakli Formation and the layer C to the Selvipinari Formation. The layer A is *Exogyra*-bearing sandstone. In the layer B fossils are absent. In some sites, submarine caves or small

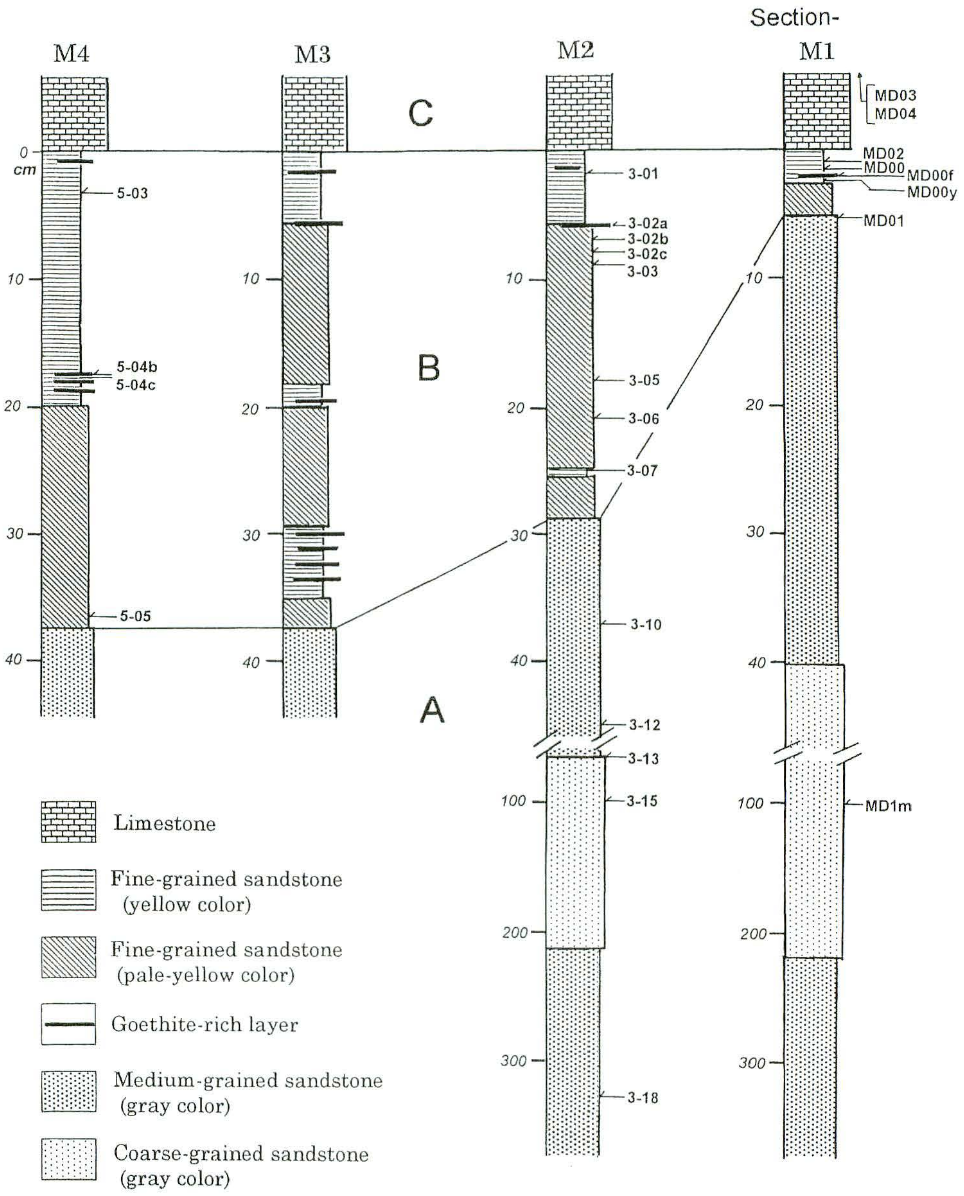

Fig. 2 Detailed cross sections and sample locations in the K-T boundary in Medetli, NW Turkey. The layer A is gray-colored medium to coarse-grained sandstone, the layer B is yellow-colored fine-grained sandstone, and the layer C is white-colored limestone. One to several goethite-rich layers (black bar) are intercalated in the layer B. The layer A is the Maastrichtian and the layer C is the early Paleocene, and the layer B doesn't occur fossils.

channels in which the limestone deposed convex downward is seen (Arakawa et al., 2003). The layer A is composed of coarse to medium grained gray colored sandstone, and *Exogyra* is found in coarse-grained sandstone layer. The layer B consists of fine-grained yellow colored sandstone and intercalated thin goethite-rich layers. Geothite-rich layers are generally thin (3 mm to 8 mm) and form layers or thin lenses within the fine-grained sandstone. One to several layers of them are parallely intercalated (Fig. 2). The layer C (Selvipinari Formation) is a white-colored limestone which contains *Laffittenina bibensis* Marie and *Mississippina* sp. (Matsumaru et. al, 1996) This limestone is more than 20 m thick. The lowest part of the limestone is all silicified. From the available biostratigraphical data, there may be a small (or major) hiatus at the boundary between the layer A and layer B and/or between the layer B and layer C. These stratigraphical and sedimentological features are different from those of well-known K-T sites (e.g., Gubbio in Italy, Stevns Klint in Denmark and Woodside Creek in New Zealand), in which the only thin clay layer exists as the K-T boundary.

PETROGRAPHY AND MINERALOGY

Fresh rock samples are collected and are checked under the microscope. We also tried X- ray diffraction measurement of powdered rock samples. The sandstone in the layer A is composed of sub-rounded quartz and feldspars and some rock fragments. The grain size is generally 0.3-0.5 mm. Polycrystalline quartz and feldspars are abundant. In X-ray diffraction, quartz, kaolinaite, illite and smectite were detected. The sandstone in the layer B is composed of 0.3-0.4 mm size quartz and feldspar grains, and goethite is also included (though not detected in X-ray measurement). Besides quartz, kaolinite and illite are also detected by X-ray diffraction. The goethite-rich layer within the layer B consists of goethite, quartz and feldspar grains. X-ray diffraction showed quartz, kaolinite, illite and goethite from this layer. As stated in Arakawa et al. (2003), shocked quartz grains, mineral or glass spherules and Ni-rich spinel, which are critical evidences for the K-T boundary layers, have not been found yet.

ANALYTICAL METHODS

We have analyzed 24 samples from three sections (section M1, M2 and M4). Major element concentrations for the samples except limestones were measured using X-ray fluorescence (XRF) spectrometer, and those for limestone samples were determined by inductively coupled plasma-atomic emission spectrometer (ICP) at the Saitama University. Detection limits for XRF method are 0.01 wt. % for all major elements, and those for ICP are better than 0.01 %. Ba, Sr, Y, Zr and V were measured by ICP method. Chromium, Co, Th, U, Cs, Hf, As, Sb and Sc were measured by instrumental neutron activation analysis (INAA) method, and Rb, Ni, Cu and Zn, and rare earth elements (REEs) were determined by inductively coupled plasma-mass spectrometry (ICP-MASS) method, both by Activation Laboratories Ltd., Canada. Detection limits for ICP and INAA, and ICP-MASS are shown in Arakawa et al. (2003). The procedure of Sr extraction from the samples is as same as Arakawa (1990). The Sr isotope compositions (^{87}Sr/^{86}Sr) were determined by Finnigan MAT 262 mass spectrometer at the Ocean Research Institute, University of Tokyo. All the ^{87}Sr/^{86}Sr were normalized to ^{86}Sr/^{88}Sr=0.1194. The measured ^{87}Sr/^{86}Sr ratios for NBS 987 standard were 0.710243 + 0.000012. The uncertainties of the ^{87}Sr/^{86}Sr ratios are estimated to be less than 0.000025 (2σ level). The age correction was made assuming the geologic time of 65 Ma for most samples except limestone samples.

RESULTS AND DISCUSSION

Element profiles of boundary sediments

Analytical results of element concentrations are shown in Tables 1-3 of Arakawa et al. (2003). Figure 3 shows a profile of Fe (%) concentration of section M2 at Medetli. The Fe concentration is generally low in layers A, B and C, but is remarkably high in the goethite-rich layer (3-02a) within the layer B. Another small peak is also seen in 3-07 sample of the layer B. For the major elements (Fig. 4), Al_2O_3, MgO, MnO, Na_2O and K_2O are slightly lower in the layer B compared with the layer A. In goethite-rich layer (3-02a), major elements show no visible peak in the profiles. Figures 5 and 6 indicate some trace element profiles in the Medetli section M2. Ba, Rb and Y, are relatively high in the layer A than in the layer B, but Sr is clearly high in the layer B. Strong peaks of Ni, Co, Cr, As and Sb (Figs. 5 and 6) are also found in a goethite-rich layer (3-02a), as for Fe concentration. Small peaks in Ni and Co are seen in 3-07. These high concentrations of Fe, Co, Ni and Cu in goethite-rich layers are generally found in the K-T boundary layers in the world (e.g., Alvarez et al., 1980; Kyte

Table 1 Rb and Sr concentrations and Sr isotope ratios of sediments in the Medetli, NW Turkey

Sample	Rb ppm	Sr ppm	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ ±($2\sigma_m$)	$^{87}Sr/^{86}Sr_i$	level cm
Section-M2						
MD04	1.4	129	0.0305	0.707898 (19)	0.70787	+95
MD03	0.6	86	0.0202	0.707882 (10)	0.70787	+15
3-01	6.0	158	0.1099	0.708107 (16)	0.70801	-2
3-02a	14.9	272	0.1585	0.708281 (11)	0.70814	-6
3-02b	20.7	214	0.2798	0.708383 (11)	0.70813	-7
3-02c	17.4	220	0.2288	0.708697 (16)	0.70849	-8
3-03	14.9	138	0.3124	0.708530 (15)	0.70824	-9
3-05	12.1	291	0.1203	0.708137 (11)	0.70803	-18
3-06	27.1	265	0.2959	0.708308 (13)	0.70804	-21
3-07	35.8	284	0.3650	0.708390 (14)	0.70805	-25
3-10	67.6	88	2.227	0.712652 (15)	0.71060	-37
3-12	70.7	84	2.438	0.712110 (18)	0.70986	-45
Section-M1						
MD00a	12.3	154	0.2311	0.708210 (11)	0.70800	-1.5
MD00f	3.5	216	0.0469	0.707939 (15)	0.70790	-2.1
MD01	52.5	106	1.4383	0.712494 (12)	0.71117	-5.3
MD10	24.4	71	0.9948	0.710777 (18)	0.70986	-100
Section-M4						
5-03	18.0	116	0.4490	0.708756 (14)	0.70834	-3.4
5-04b	13.2	264	0.1450	0.707884 (9)	0.70775	-17.4
5-04c	20.1	349	0.1671	0.707920 (15)	0.70777	-17.8
5-05	37.4	267	0.4050	0.708474 (12)	0.70810	-36.3

et al., 1980; Smit and Ten Kate, 1982; Schmitz, 1988). Concentrations of Ni (194-349 ppm) and Co (29-43 ppm) for the goethite-rich layers in this study and previous study (Arakawa et al., 2003) are in the range of those for the well-known marine K-T boundary sediments (66-1370 ppm for Ni and 7-230 ppm for Co) (e.g., Gilmour and Anders, 1989). Also high concentrations of chalcophile elements, such as As, Sb and Zn, are documented at many K-T boundary sites (e.g., Kyte et al.,

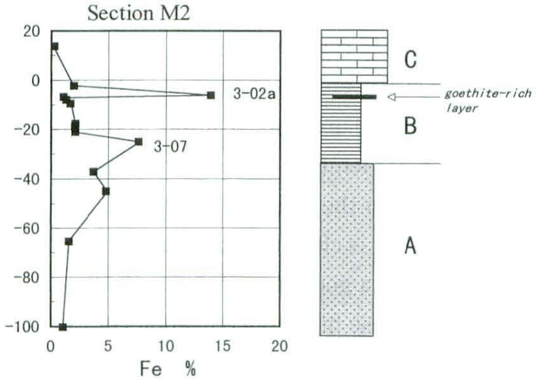

Fig. 3 Profile of Fe concentration (%) of section M2.
Sample number 3-02 is goethite-rich layer.

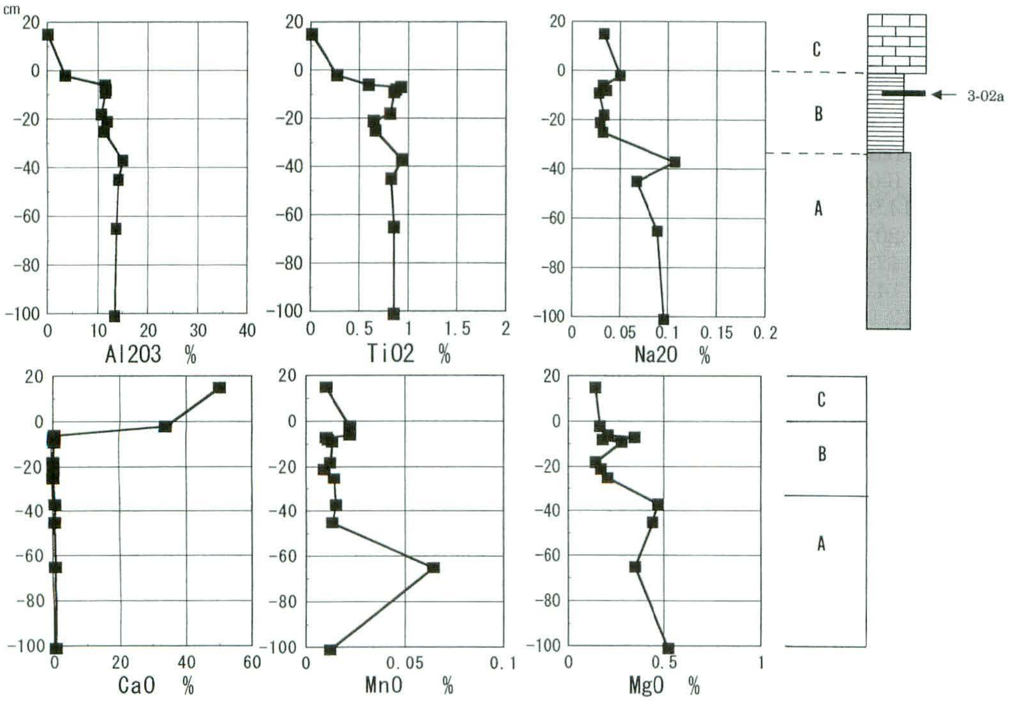

Fig. 4 Profiles of some major element concentrations in section M2.
Sample of 3-02a is goethite-rich layer.

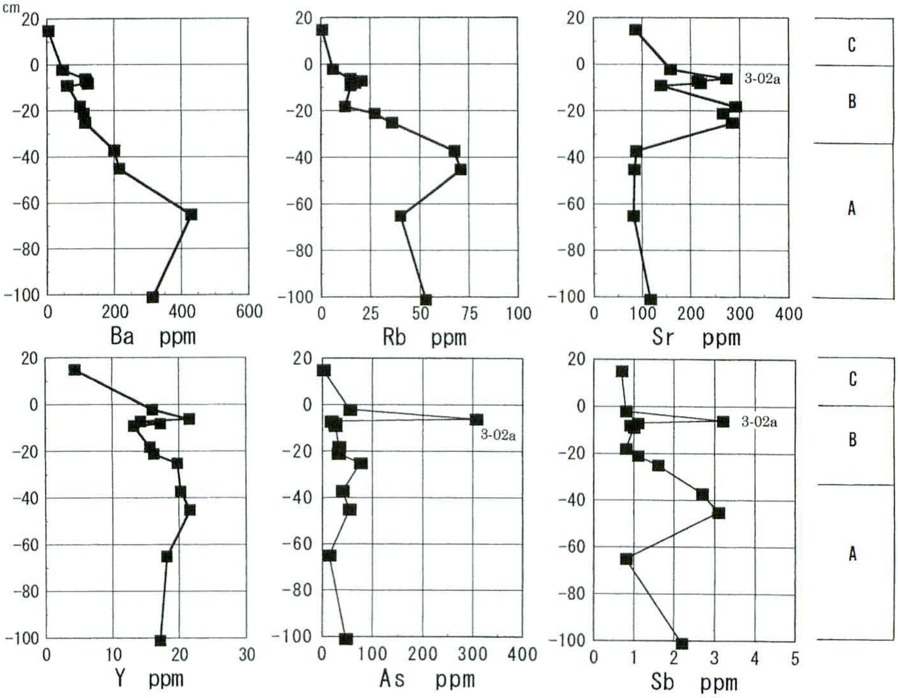

Fig. 5 Profiles of Ba, Rb, Sr, Y, As and Sb concentrations in section M2.

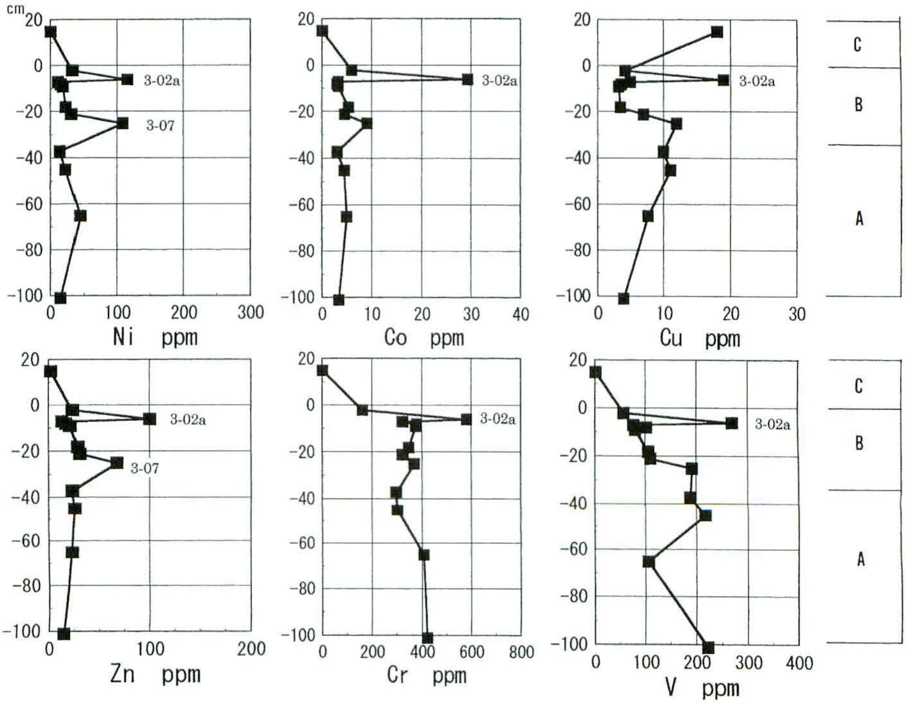

Fig. 6 Profiles of Ni, Co, Cu, Zn, Cr and V concentrations in section M2.

1980; Smit and Ten Kate, 1982; Strong et al., 1987; Gilmour and Anders, 1989; Schmitz, 1992). However, in this study high Ir concentration was not detected in the goethite-rich layers. Most are 0.05-0.10 ppb, which agree with crustal Ir concentration level. Relatively high Ir concentrations (0.24 ppb) are only measured in MD01 in the section M1. The MD-01 is a sample taken from the top of layer A (Arakawa et al., 2003) . This slightly high concentration of Ir from MD-01 suggests that the layer concentrating Ir (actual K-T boundary layer) could have been situated between the top part of layer A and the base of layer B, and that the Ir in the layer might have been diluted or eroded by successive events.

Although some change in element concentrations are visible from the layer A to the layer B (e.g., Ba, Rb and Sr), the marked change are not always seen in major and trace element concentrations.

Profiles of Sr isotope ratio

For the purpose of clarifying the chemical change in the assumed K-T transition layers in Medetli, we tried to measure the Sr isotope composition ($^{87}Sr/^{86}Sr$) of the two sections (section M1 and section M2). The initial (age-corrected) $^{87}Sr/^{86}Sr$ ratios of samples in the layer A are in the range of 0.7099-0.7112 (Fig. 7). On the other hand, the samples of layer B show relatively low $^{87}Sr/^{86}Sr$ ratios (0.7079-0.7084). Clear change of $^{87}Sr/^{86}Sr$ ratios are found between the layer A and layer B. This drastic lowering of the ratios are possibly related to the increase of Sr concentrations in the layer B(Fig. 5). This means that the Sr in the sea water more precipitated to the sandstone samples in the layer B rather than those in the layer A, because $^{87}Sr/^{86}Sr$ ratios of the sea water at the K-T boundary time (65 Ma) (0.7077-0.7078) (e.g., DePaolo and Ingram, 1985; Palmer and

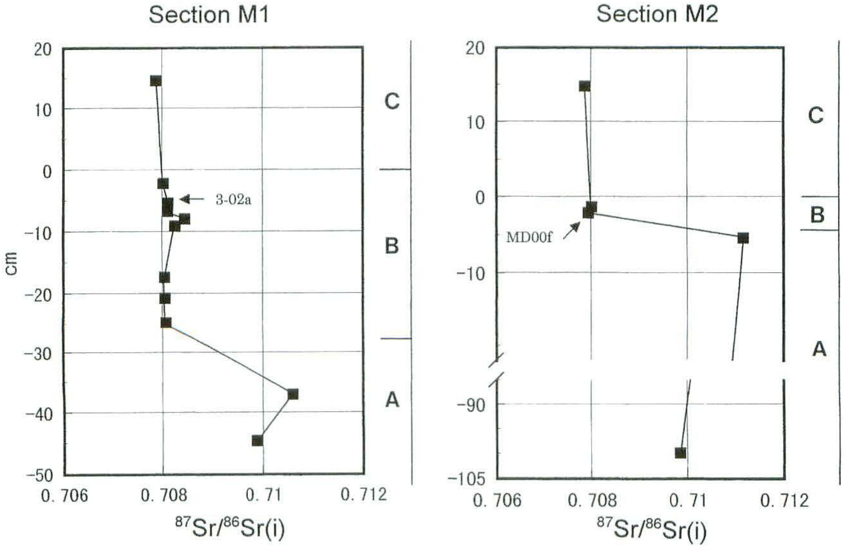

Fig. 7 Profiles of initial Sr isotope ratios (87Sr/86Sr) in sections M1 and M2. 3-02a and MD00f are goethite-rich rayers.

Elderfield, 1985) are very close to the measured ratios. The ratios of goethite-rich layers are in the range for the ratios of layer B. The ratios of layer C (limestone samples) correlate well with the ratios of early Tertiary sea water. At any rate, the drastic change of Sr isotope ratios are assumed to have occurred between the deposition of layer A and layer B. This may be another evidence that the K-T boundary exists between the layer A and layer B.

Comparison with other K-T boundary sites

Although the clear and strong evidences for the K-T boundary layer could not yet be found in the Medetli section, it is able to compare the characteristics of the boundary in Medetli to the other famous K-T boundary sites in the world.

The Medetli section in northwestern Turkey indicates some differences from those of the other K-T sites of the world. In many marine K-T sites, the thin (1-2 cm) red clay layer is intercalated between the Cretaceous and Tertiary sedimentary layers (Gubbio, Caravaca, Stevns Klint, Woodside Creek etc.). The markers evidencing asteroid impact such as the enrichment of Ir and other platinum group elements and some siderophile elements, mineral or glass spherules, shocked quartz grain are included in these thin clay layers. These results have suggested that the K-T extinction event occurred during the very short time interval (e.g., Alvarez, 1986; Wolbach et al., 1988; Gilmour and Anders, 1989). These results have reached to the single impact model in the K-T boundary time.

The Medetli K-T boundary section (actual K-T and successive layers?) may corresponds to the yellow colored sandstone layers (28-37 cm) including thin several goethite-rich layers and probably the top of the layer A, though the actual K-T boundary layer might have been thin and the most part have been eroded. The Medetli section is not similar to the sections of the well-known K-T sites. In the recent studies, it has been clear that the temporal and stratigraphic complexities in markers showing the impact of extraterrestrial materials exist during the K-T time. For example, the spherule rich layer is 60 cm lower than the Ir rich layer in the Haiti K-T section, and several peaks of Ir enrichment were found in 30 cm section in the Brazos River, Texas (e.g., Rocchia et al., 1996). The separated existence of spherule-rich layer and Ir-rich layer were documented from the Mimbral section, Mexico, and thus an extended period of time from the spherule deposition to Ir precipitation was proposed (Stinnesbeck et al., 1993).

In spite of these complexities, the recent studies have powerfully proposed that these complex temporal and sedimentological features are also explained as a result of single impact at the Yucatan Peninsula (e.g., Bohor, 1996; Smit, 1996; Smit et a., 1999) rather than the multi impact or more complex models. Although there remain some problems to research, the Medetli section, particularly the top of layer A and layer B, may be explained as a result of the same event. In this study, some other markers or evidence for the impact of extraterrestrial materials (such as shocked quartz with characteristic planar deformation features, mineral or glass spherules etc.) have not been found yet. The actual K-T boundary may be situated between the top of layer A and the bottom of layer B. Though the possibility that the real K-T boundary may have been eroded is not eliminated, the top of layer A and layer B of the Medetli section seem to have been formed during the K-T and its successive time. More works may be needed in the future.

CONCLUSION

The Cretaceous-Tertiary (K-T) transitional layers in Medetli, Gölpazari, northwestern Turkey show different stratigraphical and chemical profiles comparable to well-known the K-T boundary layers of the world. The late Maastrichtian gray colored sandstone layer (layer A) is overlain by the yellow colored sandstone layer (layer B) with thin goethite-rich layers. The lower Paleocene limestone (layer C) overlies the layer B. Fossils are absent in the layer B (28-37 cm in thickness). The major elements such as Al_2O_3, MgO, MnO, Na_2O and K_2O are slightly lower in the layer B compared with the layer A. For trace elements, Ba, Rb and Y, are relatively high in the layer A than in the layer B, while Sr is clearly high in the layer B. Strong peaks of Fe, Ni, Co, Cr, As and Sb are found in a goethite-rich layer. The initial (age-corrected) $^{87}Sr/^{86}Sr$ ratios of samples in the layer A are in the range of 0.7099-0.7112, while the layer B show relatively low $^{87}Sr/^{86}Sr$ ratios (0.7079-0.7084). This drastic change of Sr isotope ratios is explained by a drastic increase of precipitation rate of the sea water Sr to the layer B rather than in the layer A. This change may be related to the K-T event. Combined with these results and previous data (Arakawa et al., (2003), the actual K-T boundary is situated probably between the top of layer A and the bottom of layer B. In the Medetli region, the deposition of the top of layer A and probably the layer B are considered to have been formed by the K-T and its successive events.

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