Vertical Variation of Rhenium, Cadmium, Silver and Platinum-group Elements within a Transitional Bed of Danish Cretaceous-Tertiary Boundary Layer

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Abstract : Contents of Re, Cd, Ag and platinum-group elements in specimens from four sub-zones of a 3 cm-thick bed of a K-T boundary layer from Stevns Klint in Denmark, were determined by stable isotope dilution using ICP mass spectrometer. The chondrite-normalized Re value linearly decreases in the upper zone. Also the content of Ag linearly diminishes upward. These relations lead us to a conclusion that, at the earliest stage of the formation of this bed, the marine site studied was highly reducing, and at the final stage of the bed formation, the sea recovered to the "normal" oxidation-reduction potential. That is, it is reasoned that the anomalously reducing condition at the site persisted for a relatively short period. Some discussions are given to effect of chemical valency state on distributional features and to fractionation in the dust fallout.

Key words : K-T boundary; oxidation-reduction potential; rhenium; silver; PGE.

The Cretaceous-Tertiary geological boundary corresponding to a time of sudden extinction of species on earth is one of the highly intriguing targets of geochemical researches. Since the proposal of meteorite impact theory¹⁾ endorsed by high contents of Ir in the boundary samples, the majority view has favored the impact theory subsequently consolidated by the identification of a potential impact site.²⁻⁴⁾ A scenario involving a combination of both the impact theory and volcanism theory⁵⁾ has also been suggested.⁶⁾

It is important to study the K-T boundary samples from a wide variety of sites covering the earth in order to compare the events. It is also highly significant to carry out a vertical systematic investigation of a boundary layer which has been preserved with little disturbance, by considering a number of platinum-group elements and some chalcophile elements. The samples from Stevns Klint, Denmark, can be regarded well preserved and, therefore, suitable for investigation. It is desirable to obtain high-quality data for the elements analyzed in order to present accurate results

and to make sound judgment and draw good conclusions for this study.

Samples. The specimens we investigated are from a thin marl layer at the base of the Danian, occurring in small basins between the Cretaceous white chalk and the overlying calcareous Tertiary formations. According to Christensen *et al.*,⁷⁾ the Danish K-T boundary layer at Stevns Klint is subdivided to four beds which will be here designated as beds *a*, *b*, *c*, and *d* from bottom to the top. These beds, *a*, *b*, *c*, and *d* correspond to beds, II, III, IV and V in the paper by Christensen *et al.* The bed *b* has dark brown color due to weathering of the pyrite concentrations.⁷⁾ Aikawa⁸⁾ observed that sample from this bed reacts very slowly with HCl, and lots of insoluble material remain after reaction.

The bed *c* overlying bed *b* shows gradual change in color, from slightly-brownish gray at the bottom to light gray on top. The reaction with HCl increases upward.⁸⁾ The carbonaceous residue after (HF+HClO₄) treatment decreases evidently upward.⁸⁾ The bed *c* exhibits an internal systematic zoning. Therefore this bed can be regarded to represent an interesting transition zone. We were provided with the bed *c* subspecimens, at levels 0-0.5, 0.5-1.0, 1.0-2.0, and 2.0-3.0 cm, where 0 cm refers to the boundary

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between beds *b* and *c*. Accordingly, the subspecimen at level 0–0.5 cm is the sample collected from a vertical position, 0 to 0.5 cm above the boundary between *b* and *c*.

Experimental. Recently, Yi and Masuda developed a method⁹⁾ for simultaneous determination of platinum-group elements (PGE), Ru, Pd, Ir and Pt at ultra trace levels by isotope dilution using an ICP mass spectrometer. We found later that the same procedure applied to PGE can enable us to determine simultaneously Ag, Cd and Re in addition to PGE.

An outline of the chemical treatment is as follows. Put the pulverized sample (~0.8 g) and the alkali reagent mixture for alkali fusion (KNO₃: Na₂O₂: NaOH = 3:1:1; 3–4 times the sample weight) into a zirconium crucible. Dissolve the fusion product by 6M HCl. To promote the isotopic homogenization¹⁰⁾ of Ir, digest the solution in a microwave oven after addition of chlorinated lime. Adsorb Re, Cd, Ag and PGE on anion exchange resin column and elute by a (HCl+HClO₄) mixture.

The analysis of mass spectra obtained by ICP mass spectrometer requires some caution. Note that the spectra due to ZrO⁺ and Mo⁺ cover the mass range as Cd⁺, Ru⁺ and Pd⁺. One has to pay attention to the isobaric interferences shown in Table I. From our experience, “false” peaks appear at mass numbers 100 and 101. However, we succeeded in determining Ru by solving the simultaneous equations for *m/e*=102 and 104. For determination of the elements under consideration by means of stable isotope dilution, we employed the enriched isotopes, ⁹⁹Ru, ¹⁰⁵Pd, ¹⁰⁷Ag, ¹¹¹Cd, ¹⁸⁵Re, ¹⁹¹Ir, and ¹⁹⁶Pt.

Results. *General.* We present the results of our determination in Table II. Fig. 1a shows the vertical variations in the contents of elements using a logarithmic scale of simple concentration, while Fig. 1b depicts the vertical profile of corresponding chondrite-normalized values.

Rhenium. Of the elements studied, Re shows relatively the greatest variation within bed *c*, obviously decreasing from the lower to the upper part (see Figs. 1b and 2). This indicates that, during the formation of bed *c*, the environment changed rapidly and nearly “linearly” from anoxic to oxic. It should be noted that Re (VII) and Re (IV) are chemically common and their stabilities are sensitive to the oxidation-reduction potential, and that whereas ReO₂ is insoluble in water, Re₂O₇ is soluble as perrhenate ion ReO₄[−]. Disulfide ReS₂ is also insoluble, except in hot nitric acid. It is conceivable that ReS₂ is relatively concentrated in pyrite FeS₂. It is known that, in 3.5–10 M HCl solution saturated with H₂S, ReO₄[−] precipitates as Re₂S₇. However, a chemical environment similar to this would be difficult to realize by reduction of the marine sulfate ion to sulfide ion. If a supply of concentrated H₂S from some source is invoked, it would simultaneously affect the vertical variation of Ag and Cd more drastically than observed.

In Fig. 3 the Pd-based chondritic ratio-normalized value (PCRN value) is plotted as a function of the vertical position. It is interesting to note that three points for Re fall on a straight line. Extrapolation of the straight line gives a PCRN value of 5.0 at 0 cm. We have examined the values for the data on six Stevns Klint samples analyzed by Kyte *et al.*¹¹⁾ It is worth while to note that the greatest PCRN values for Re obtained from their data are 4.75 and 5.08, in good agreement with the value estimated by the extrapolation. The values 1.83–3.67 for the other four samples appear to correspond to intermediate portion of bed *c*. According to the relation in Fig. 3, the Re content for 0–0.5 cm is estimated to be 12.75 ppb, giving a chondrite-normalized value of 0.34.

Silver. Our examination of the data published by Elliot *et al.*⁵⁾ for Ag in bed *c* (D series in the original paper) has led us to a finding that the silver content in black fissile clay varies linearly with the relative

Table I. Isobaric interferences for mass range from 96 through 113

<i>m/e</i>	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113
Mo	○	○	○		○													
Ru	○		○	●	○	○	○		○									
Pd							○		○	●	○		○		○			
Ag												●		○				
Cd											○		○		○	●	○	○
ZrO											○	○	○		○		○	

Solid circle indicates isotope for which enriched isotope was added as a spike.

Table II. Distribution of Ru, Pd, Ag, Cd, Re, Ir and Pt (ppb) in vertically sub-divided specimens from a bed *c* of K-T boundary at Stevns Klint, Denmark

Relative distance* (cm)	Ru	Pd	Ag	Cd	Re	Ir	Pt
0.0~0.5	53.4	47.3	801			78.9	54.5
0.5~1.0		43.3		4716	9.33	30.0	43.3
1.0~2.0	39.1	38.5	461	4321	4.99	27.2	39.7
2.0~3.0	19.0	31.9	339	3797	0.443	5.67	
Orgueil***	687	618	540	1100**	37**	489	1010

* From the boundary between beds *c* and *b* (cf. text).

** From ref. 12.

*** C1 chondrite.

position in the bed. We have tried to match the position of our samples with those studied by Elliot *et al.* The bed *c* studied by Elliot *et al.* was assumed to have a thickness of 30 mm as a whole and to have been cut into seven whole-rock samples with the same thickness. Fig. 4 shows the relationship between the Ag content and the relative distance. It can be seen that our determinations for 0~0.5 and 1~2 cm specimens match the alignment of the points (solid circles) representing the Elliot data,⁵⁾ but our determination for the 2~3 cm sample deviates from such an orientation. It is important to note that this deviation may be due to a fortuitous micro-local enrichment of Ag in the specimen analyzed.

Further, the linear alignment of points plotted in Fig. 4 is also interesting by considering the fact that

the extrapolation of a straight line gives a very low value of nearly zero ppb of Ag at the 30 mm level. Note that, on account of the Pd abundance (31.9 ppb) for 2~3 cm, the corresponding chondritic Ag value is 27.9 ppb. The highest Ag end portion corresponding to 0 cm can be interpreted to represent a phase enriched in metallic and/or sulfide silver precipitated from seawater owing to the highly anoxic environment. Elliot *et al.*⁵⁾ reported existence of rust-stained material (50 mg) highly enriched in all noble metals, especially Ag and Pt. The linear relationship (Fig. 4) observed would suggest a rapid recovery of the oxidation-reduction potential to the normal condition, in harmony with the inference from Re.

Cadmium. Three determined points fall very closely on a line by plotting the concentration against the depth. An extension of this line yields 4975 ppb for a 0~0.5 cm specimen. An interpolation between 0~0.5 and 1~2 cm values for Ag gives 665 ppb for a 0.5~1 cm specimen. Thus the Cd/Ag ratios for 0~0.5, 0.5~1, 1~2, and 2~3 cm specimens turn out to be 6.21, 7.09, 9.37, and 11.20, respectively. It is significant that these ratios range between 2.04 (=1100/540) for Orgueil,^{12),13)} and the average ratio for seawater,¹⁴⁾ 22.5, and that the ratio increases upward, approaching the seawater value. If the Ag content determined by us for the 1~2 cm specimen is replaced by the corresponding value, 175 ppb, estimated from the rectilinear relationship in Fig. 4, the Cd/Ag ratio will be 21.7. The little variation of Cd may be due to the

Fig. 1. a, Relationship between elemental abundances (logarithmic scale) in bed *c* and vertical relative distance (cm). b, Relationship between chondrite-normalized abundance ratios (logarithmic scale) and vertical relative distance (cm).

Fig. 2. Relationship between chondrite-normalized abundance ratios (ordinary scale) and vertical relative distance.

Fig. 3. Relationship between $(C_M/C_{Pd})_s / (C_M/C_{Pd})_0$ and vertical relative distance, where $(C_M/C_{Pd})_s$ refers to the abundance ratio between element *M* and Pd in the specimen and $(C_M/C_{Pd})_0$ to the corresponding ratio in the Orgueil meteorite.

fact that it is rather insensitive to oxidation-reduction potential. Also Cd^{2+} ($r=103$ pm) and Ca^{2+} ($r=106$ pm) have similar radii and are isovalent, thus facilitating ionic replacement in sediments.

The chondrite-normalized values for Ag and Cd and the abundance ratio of Cd to Ag at the bottom of bed *c* would provide a constraint on the original source of chalcophile elements and/or the nature of the potential primary event. We notice that the Cd/Ag ratio at the base is 3 times higher than in the carbonaceous chondrite, and the chondrite-normalized

Fig. 4. Relationship between the content of Ag and the vertical distance. The solid circles refer to the points from data of Elliot *et al.*⁵⁾ and the open circles to the points from our determination.

values of Ag, and Cd for this position are higher than unity.

Platinum group elements. Each of the four platinum group elements appears to show characteristics depending on their relative positions and the chondrite-normalized values (see Fig. 1b and 3). Platinum is characterized by relative depletion to other PGE. As compared with Pd, platinum content ratio is 0.6–0.7. A similar tendency is observed in the data presented by Kyte *et al.*¹¹⁾ With the exception of one specimen (PCRN value = 1.14), the values for the other five cases range from 0.88 to 0.61. This relative depletion of Pt can be explained in terms of a possible formation of stable chloro-complexes $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ in the presence of chloride ion in seawater. To check this interpretation, it is desired to examine non-marine K-T boundary samples. Abundance of Pd shows the least relative change from the bottom to the top. One of the possible reasons for little content variation of Pd in the bed studied may be that Pd can be stable as a divalent ion ($r=86$ nm), i.e., isovalent with Ca^{2+} . Also note that the oxidation state of Pd (IV) is not as stable as Pt (IV). From Fig. 2, the chondrite-normalized value for Ir is the highest in 0–0.5 cm, while that in 2–3 cm is the lowest among PGE. The features displayed by Ru appear to be intermediate between Pd and Ir.

When the projectile entered the earth's atmosphere, it must have been subjected to a great impact and a sudden heating. Subsequently, break-up, volatilization and pulverization must have taken place

dynamically in a great fireball. Almost simultaneously, oxidation and condensation may also have occurred under heterogeneous physical and chemical conditions. A potential main body, big brecciated fragments and big grains fell on the earth within a short time interval, while fine dusts remained transiently in the atmosphere and continued to fall out. The bed *c* can be interpreted to have been deposited during the last stages of this scenario.

One can consider that the distributional features of PGE in bed *c* reflect the original dust formation process, the size distribution of dust particles, the difference in chemical states of the elements, the differential behavior of dusty particles during their stay in the atmosphere, their chemical reaction with seawater and their chemical states trapped in sediments. These processes can give rise to fractionation among PGE as observed in the bed *c*. The least variation of Pd, i.e., a relatively stable supply of Pd may be ascribed partially to the higher fraction of the primarily formed oxide compound PdO ($d=8.3$), because metallic Pd has a density of 12.2 and the lower density is favorable for a long and stable residence in the atmosphere if the grain size is similar to each other, probably resulting in the delayed fall-out. As discussed above, the oxidation state of Pd (II) is favorable for ionic fixation in CaCO_3 . An alternative interpretation of the distributional features of Pd in the bed *c* may be homogenization by remobilization.¹⁵⁾ This interpretation, however, is open to questioning, taking into account the behavior of Re and Ag. In connection with the oxidized state of PGE, the possible presence of Os as a gaseous compound OsO_4 is worth pointing out. In the discussion of fractionation between Ru and Ir, Evans *et al.*¹⁶⁾ suggested some complicated parameters. However, it is likely that rhenium and silver have been mostly retained in a pyrite phase, while palladium and cadmium were incorporated into calcium carbonate and/or a silicate phase and remobilized to be nearly homogeneous in the 3 cm thick bed. Most of Ir is inferred to have remained in metallic or alloy dust in the sediment. If Ir was not mobilized after deposition, the results suggest that Ir dust was still faintly drizzling even after the redox potential of the sea nearly came back to normal.

As mentioned above, at the earliest stage of formation of the bed *c*, the basin in which it was formed had been too reducing for common life to survive. Therefore, it is reasoned that the calcium carbonate of the bed *c* was not produced in situ by biological processes. There can be two possible sources for carbon dioxide to produce CaCO_3 . One is CO_2 produced by forest fires.¹¹⁾ The other is CO_2 biologically emitted at some places far away⁶⁾ from Denmark.

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References

- 1) Alvarez, W., Alvarez, L. W., Asaro, F., and Michel, H. V. (1980) *Science* **208**, 1095–1108.
- 2) Swisher, C. C., III, Grajales-Nishimura, J. M., Montanari, A., Margolis, S. V., Claeys, P., Alvarez, W., Renne, P., Ceddilo-Perdo, E., Maurasse, F. J. -M. R., Curtis, G. H., Smit, J., and McWilliams, M. O. (1992) *Science* **257**, 954–958.
- 3) Sharpton, V. L., Dalrymple, G. B., Marin, L. E., Ryder, G., Schuraytz, B. C., and Urrutia-Fucugauchi, J. (1992) *Nature* **359**, 819–821.
- 4) Blum, J. D., Chamberlain, C. P., Hingston, M. P., Koeberl, L. E., Marin, L. E., Schuraytz, B. C., and Sharpton, V. L. (1993) *Nature* **364**, 325–327.
- 5) Elliot, W. C., Aronson, J. L., Millard, H. T., Jr., and Gierlowski-Kordesch, E. (1989) *Geol. Soc. Am. Bull.* **101**, 702–710.
- 6) Sutherland, F. L. (1994) *Earth-Sci. Rev.* **36**, 1–26.
- 7) Christensen, L., Fregerslev, S., Simonsen, A., and Thiede, J. (1973) *Bull. Geol. Soc. Den.* **22**, 193–212.
- 8) Aikawa, M. (1992) Master Thesis, Univ. Tokyo.
- 9) Yi, Y. V., and Masuda, A. (1996) *Anal. Chem.* **68**, 1444–1450.
- 10) Yi, Y. V., and Masuda, A. (1996) *Anal. Sci.* **12**, 7–12.
- 11) Kyte, F. T., Zhou, Z., and Wasson, J. T. (1980) *Nature* **288**, 651–656.
- 12) Mason, B. (ed.) (1971) *Handbook of Elemental Abundances in Meteorites*. Gordon and Breach, New York.
- 13) Yi, Y. V., Masuda, A., Aikawa, M., and Ganapathy, R. (1995) *Proc. Japan Acad.* **71B**, 279–282.
- 14) Nozaki, Y. (1985) *Chikyu-kagaku* **19**, 59–64.
- 15) Evans, N. J., Gregoire, D. C., Goodfellow, W. D., McInnes, B. I., Miles, N., and Veizer, J. (1993) *Geochim. Cosmochim. Acta* **57**, 3149–3158.
- 16) Evans, N. J., Ahrens, J. T., and Gregoire, D. C. (1995) *Earth Planet. Sci. Lett.* **134**, 141–153.