Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 77 (2) 247–255 (2012) UDC 550.4:597+56.022:551.352.1:552.63(489)
JSCS–4265 *Original scientific paper*

Iridium anomaly in the Cretaceous–Paleogene boundary at Højerup (Stevns Klint, Denmark) and Woodside Creek (New Zealand): the question of an enormous proportion of extraterrestrial component

PAVLE I. PREMOVIĆ[1]*, BUDIMIR S. ILIĆ[2] and MILOŠ G. ĐORĐEVIĆ[1]

[1]*Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, University of Niš, P. O. Box 224, 18000 Niš, Serbia and* [2]*Department of Pharmacy, Faculty of Medicine, University of Niš, 18000 Niš, Serbia*

(Received 4 April, revised 8 August 2011)

Abstract: The Cretaceous–Paleogene boundary clays at Højerup and Woodside Creek show anomalous enrichments of iridium compared with the marine sedimentary rocks. For the average iridium content of 465 ppb in CI chondrite the estimate of the carbonaceous chondritic proportions in the decarbonated iridium-rich boundary layers, based on the integrated iridium fluencies, is about 26 % at Højerup and 65 % at Woodside Creek. These proportions are most likely too high due to a significant Ir influx from the nearby marine or continental site to these sections.

Keywords: Fish Clay; Woodside Creek; iridium; carbonaceous chondrite.

INTRODUCTION

In the original paper, Alvarez *et al.*[1] first reported anomalously high Ir concentrations in the Cretaceous–Paleogene (KPB) boundary clays at Højerup (eastern Denmark, Fig. 1) and at Woodside Creek (the northern part of the South Island of New Zealand, Fig. 1). They proposed an impact of an extraterrestrial bolide to explain the elevated Ir content at the KPB. In general, Ir and other platinum-group elements (PGE: collectively the elements Ru, Rh, Pd, Os, Ir and Pt) are invariably enriched in the prominent KPB clays. Other trace elements (*e.g.*, heavy metals) are also relatively abundant in these clays.

Many researchers consider that the KPB impactor formed the *ca*. 180 km crater at Chicxulub (Yucatan Peninsula, Mexico). It was suggested that the impactor was a carbonaceous chondrite-type body,[2–6] although it is still unclear whether it was a carbonaceous chondrite or a comet. Indeed, comets are believed to be primitive bodies with a composition similar to that of carbonaceous chon-

* Corresponding author. E-mail: pavle.premovic@yahoo.com
doi: 10.2298/JSC110404178P

drites.[7] The anomalous Ir associated with the prominent boundary clay is, however, consistent with the high Ir content typical of most chondritic meteorites and inconsistent with the general proposition of comets. Indeed, a simple calculation shows that in the case of ice-rich comets (>70 % ice, *e.g.*, the Haley-Bopp comet), the amount of iridium produced by an impact energy for a crater of the Chicxulub size could be less than 0.001 % than that of an asteroid.

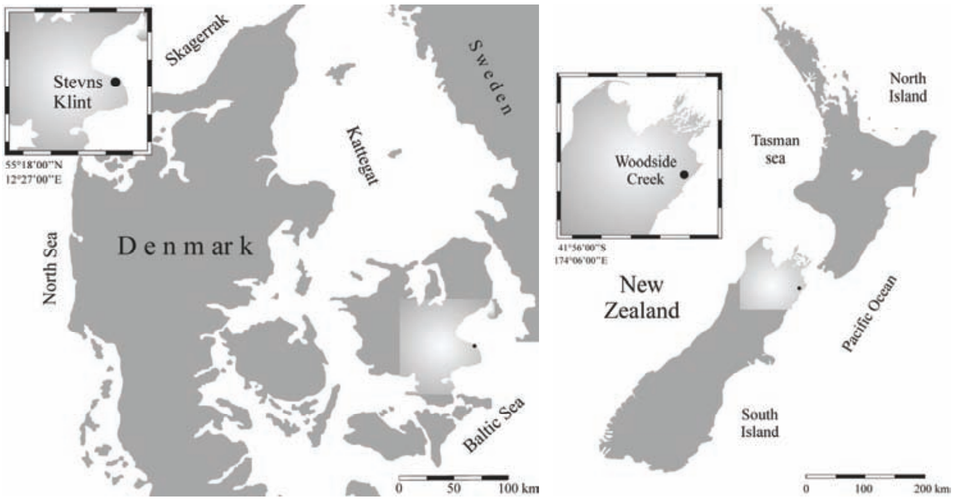

Fig. 1. Geographic location of Stevns Klint in Denmark and Woodside Creek in New Zealand.

In the past, many researchers used the iridium concentration and/or integrated amount of iridium to estimate the proportion of chondritic component in the renowned boundary clays. This brief paper aims to re-examine this method using comprehensive Ir data from the sites at Højerup and Woodside Creek, which are available and were published by Schmitz.[8]

RESULTS AND DISCUSSION

Fish Clay. The lowermost Danian Fish Clay Member of the Rødvig Formation near the village of Højerup is a classic marine KPB section. The lithology of the Fish Clay within this boundary section characterizes four distinctive layers: black-to-dark marl (hereinafter BDM) with a basal red (goethite-rich) layer, brown-to-grey marl and at the top light-grey marl (Fig. 2). The red layer is underlain by (latest) Maastrichtian bryozoan-rich limestone, whereas the top marl is overlain by (early) Danian Cerithium limestone.[8–12] Geochemical studies show that the Ir profile (on a whole rock basis) across the Fish Clay column is characterized by a sharp maximum in the base of the BDM with an upward gradual decrease (tailing-off) from its maximum (*e.g.*, Schmitz[10]). The BDM is considered to constitute the main part of the boundary section, since it probably contains more than 95 % of the total Ir in the Fish Clay.[13] The mineralogy of the BDM is comparatively simple, smectite and authigenic (mainly biogenic) calcite being the principal components. Geochemical evidence indicates that the BDM was deposited under strong anoxic conditions but the red layer under strong oxic sedimentation conditions.[13]

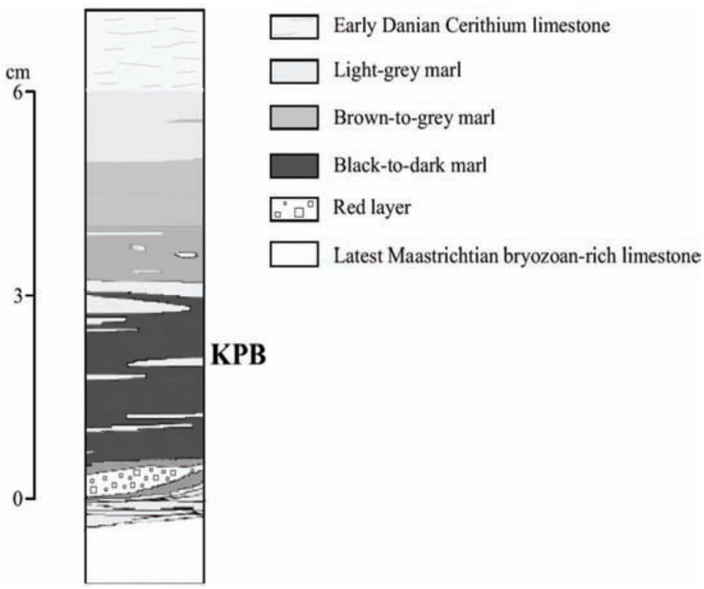

Fig. 2. Expanded lithological log of the Fish Clay at Højerup, based on Surlyk *et al.*[12]

As pointed out above, the Ir enrichment of the KPB clays is generally regarded as indicative of the presence of a carbonaceous chondrite (CC) component. Table I shows that carbonaceous chondrites typically contain 406.0–849.4 ppb Ir, while, on average, marine sedimentary rocks usually contain below 1 ppb (Table I); hence, little addition of a CC component would be necessary to critically increase the concentration of Ir in a marine sedimentary rock. Thus, Ir is a very sensitive means of examining the CC contribution to marine KPB clays such as the Fish Clay. Some authors suggested that Ir in the Fish Clay was sourced by iridium from seawater. However, the average iridium concentration in the decarbonated BDM (100 ppb) represents an enrichment factor of about 10^{17} compared to seawater (*ca*. 2×10^{-15} ppb, Table I). Moreover, according to these authors, the residence time of iridium in the oceans is about 1 million years. Thus, the excess of Ir in the BDM, therefore, could not have been derived from a sea reservoir.

Kyte *et al.*[14] estimated that the extraterrestrial component in the basal 1-cm part of the BDM from the measured Ir concentration (47.4 ppb) is about 10.5 %, corrected for about 20 % carbonate content. According to Grieve,[15] the chondrite-normalized relative abundance of Ir indicates that the Fish Clay (on a whole-rock basis) contains an admixture of about 10 % chondrite. Trinquier *et al.*[6] showed that the Cr isotopic signature of the BDM represents a mixing of the CC matter with terrestrial material in a ratio of up to 6.8 %. Recently, Osawa *et al.*[16] estimated from the measured Ir concentration (29.9 ppb) that the extraterrestrial material in the basal part of BDM was diluted 1/19 (on a whole-rock basis), assuming that the Ir concentration of CC is 470 ppb. Of note, an impactor mass fraction globally dispersed after the Chicxulub impact ranged between 22[1] to 50 %.[17]

TABLE I. Concentrations of Ir in carbonaceous chondrites, marine sediments and seawater

Specimen		Ir content, ppb
Carbonaceous chondrites	Maximum	849.4[a]
	Minimum	406.0[a]
Marine sediments		<1[b]
Seawater		2×10^{-15}[c]

[a]Walker[29]; [b]Anbar *et al.*[30]; [c]Goldberg *et al.*[31]

Schmitz[8] reported instrumental neutron activation analysis (INAA) data for Ir in the carbonate-free fraction across the Fish Clay (Fig. 3a) as this metal is

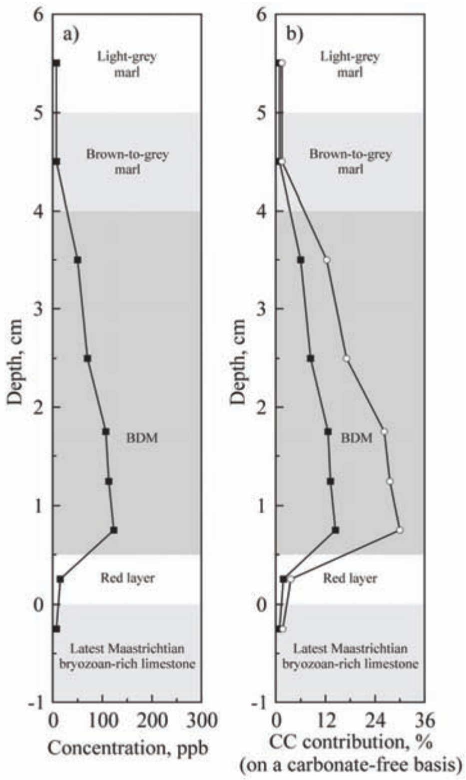

Fig. 3. a) Concentration profiles of Ir (on a carbonate-free basis) in the Cretaceous–Paleogene boundary clays at Højerup (Fish Clay). The samples were analyzed by instrumental neutron activation (INAA). The relative error in the precision of the analyses ranges from 5 to 10 %. The total uncertainties (including accuracy errors) were up to 20 %.[8] b) The CC contributions for the decarbonated Fish Clay based on the Ir concentrations. Lowest (■) and highest (○) CC contributions were calculated assuming that the Ir content of the carbonaceous chondrite was 406.0 and 849.4 ppb, respectively (Table I).

wholly located in this fraction. This profile shows that the peak and mean concentrations of Ir in decarbonated BDM is about 120 and 100 ppb, respectfully. Using these data and assuming that all the Ir found in the Fish Clay originated from the CC component, it was estimated that the decarbonated BDM is derived from about 6–30 % CC (Fig. 3b). This estimate assumed that the Ir content of the carbonaceous chondrites range from 406.0 to 849.4 ppb, Table I. If 465 ppb represents the average content of Ir in CI chondrites[18] then the CC contribution to the decarbonated BDM averages about 21 %.

A better measure of an Ir anomaly in boundary clay is the integrated Ir fluence. This fluence for the carbonate-free BDM (assuming a density of 2 g cm^{-3}) was estimated at about 600 ng cm^{-2} after integration in the interval from 0.5 to 4.0 cm. For comparison, an estimate of the Ir fluency for the global impact deposit for the KPB is about 40–55 ng cm^{-2}.[19] This value corresponds approximately to about 700 to 1500 mg cm^{-2} CC, based respectively on 406.0 to 849.4 ppb Ir in carbonaceous chondrites (Table I). These estimates correspond to about 14––30 % CC in the decarbonated BDM; for an average Ir content of 465 ppb in CI chondrite, the contribution is about 26 %. Such a significant proportion of CC, however, is not supported by any mineralogical evidence. Indeed, if initially the precursor material of BDM contained a high percentage of impact-derived ejecta fallout, then diagenetic alteration would have left a residue with high concentrations of the impact-derived markers. To the best of our knowledge, the BDM contains no altered meteoritic fragments[20] and only about 0–6 shocked quartz grains per gram.[21] On the other hand, similar calculation based on Ir fluency indicates that the underlying reddish layer (with 15. 2 ppb of Ir, Fig. 3a) contains as low as about 3.3 % of CC material. In sharp contrast, this layer is abundant with well-preserved, impact-related goethite-rich microspherules[10,22] and with nano--size goethite grains,[20,23] interpreted as altered meteorite fragments.[20] About 29––33 shocked quartz grains per gram were also identified in this layer.[21] Of note, the total iridium flux of the carbonate-free Fish Clay is about 615 ng cm^{-2}, which corresponds to about 27 % CC for an average Ir content in the CI chondrite of 465 ppb.

The present estimation (judging from the Ir concentrations and fluence) may substantially underestimate the actual CC contribution to the decarbonated BDM. There are two reasons for this. The anomalous amounts of Ir in the decarbonated Fish Clay display a gradual decrease from the BDM upwards but this metal is still relatively elevated (<5 ppb) in the light-gray marl (Fig. 3a). These stratigraphically extended enrichments of Ir may be explained by redox-controlled remobilization.[24] In addition, according to Peucker-Ehrenbrink and Hanningan,[25] between about 40 and 80 % of the initial Ir budget could have been lost due to surficial weathering of black shales (such as BDM) within roughly 13,000 years. Thus, because of the assumed remobilization and/or weathering loss of Ir, the original proportion of CC in the carbonate-free part of the BDM could actually be even considerably higher than presented above. A more detailed discussion of this issue is beyond the scope of this paper.

The CC matter (and associated Ir) could have been deposited in the Fish Clay by the direct airborne ejecta fallout settling through the seawater column or transport from the nearby marine or continental site to the Fish Clay bed. Kyte *et al*.[14] reasoned that Ir (and other siderophiles) in the basal 1-cm-thick part of the BDM is only representative of primary Ir derived from the initial ejecta fallout deposited during a short time (a few days, months or years) after the impact. According to these researchers, Ir above this layer is probably secondary in origin and transported from the original nearby site, which increased the primary Ir values. Wolbach *et al*.[26] proposed that secondary Ir is ejecta material eroded from marine elevated sites to topographic lows already containing some primary fallout. Premović[13] has suggested that Ir in the Fish Clay was probably fluvially transported from the soil on the adjacent land and redeposited in a shallow marine basin at Højerup. This author argued that a predominant part of the Ir in the BDM ultimately came from CC material associated with ejecta fallout covering the nearby coastal soil. Consequently, overestimated proportions of the CC matter in the decarbonated BDM are probably due to the high Ir input from a marine or continental site.

The Woodside Creek section. The KPB at Woodside Creek is represented by a reddish goethite-rich clay layer that is up to 1-cm thick. The boundary clay at Woodside Creek (BW) is underlain by Maastrichtian siliceous limestone and overlain by siliceous claystone,[27] Fig. 4. Previous sedimentary studies showed that this clay (see for example)[28] is not primary fallout but redeposited (a feature that is difficult to reconcile with the high Ir anomaly) and affected by erosion or non-deposition. These studies also imply that the BW was deposited in a shallow marine region under well-oxygenated conditions.

Schmitz[8] also reported INAA data for Ir in the carbonate-free BW (Fig. 4a). Of note, the Woodside Creek sections also shows an Ir "tailing effect" as does the Fish Clay, but it is less pronounced, Fig. 4a.

Figure 4a shows that the peak concentration of Ir in the decarbonated BW is 460 ppb, which is one of the highest measured to date for any KPB interval. Using this data and assuming that all the Ir found in this boundary section originnated from the CC component, it was estimated that the decarbonated BW is derived from about 60 % up to bizarre 115 % CC (Fig. 4b). If 465 ppb represents an average content of Ir in CI chondrites[18] then the CC contribution to the decarbonated BW averages about >100 %.

The integrated Ir fluence for the carbonate-free red layer of the BW (assuming a density of 2 g cm^{-3}) was estimated at about 600 ng cm^{-2}**,** after integration in the interval from 0 to 1 cm, which is (fortuitously?) identical to that estimated for the BDM. This value corresponds, as for the BDM case, to approximately 700 to 1500 mg cm^{-2} CC based on 406.0 to 849.4 ppb Ir in carbonaceous chondrites (Table I). These estimates correspond to about 35–75 % CC in the decarbonated BW. For an average Ir content of 465 ppb, the CI chondrite contribution to this decarbonated section is 65 % CC.

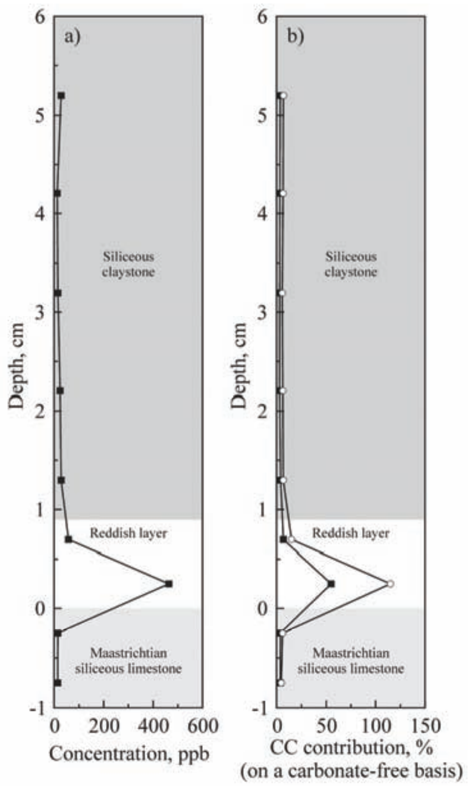

Fig. 4. a) The Ir concentration profile (on a carbonate-free basis) across the Cretaceous–Paleogene boundary section at Woodside Creek. The samples were analyzed by instrumental neutron activation (INAA). The relative error in the precision of the analyses ranges from 5 to 10 %. The total uncertainties (including accuracy errors) were up to 20 %.[8] b) The CC contributions for the decarbonated boundary section at Woodside Creek based on the Ir concentrations. Lowest (■) and highest (○) CC contributions are calculated assuming that the Ir content of the carbonaceous chondrite was 406.0 and 849.4 ppb, respectively (Table I).

As in the case of BDM, a high percentage of the impact-derived ejecta fallout would have left a residue after diagenesis with high concentrations of the impact-derived indicators in the BW. To the best of our knowledge, this thin reddish layer contains numerous (possibly?) impact-derived goethitic microspherules and about 2–8 shocked quartz grains per gram were identified in this layer.[21]

In analogy to the Fish Clay, it is assumed that the Ir in the BW probably originated from a carbonaceous chondritic component of ejecta fallout deposited on nearby adjacent land or marine area.

Assuming that 50 % represents the CC fraction in ejecta fallout (with an average density of about 2 g cm^{-3}), then about 0.7–1.5 g of the ejecta fallout would have sourced almost all the integrated amount (*ca*. 600 ng cm^{-2}) of Ir in the decarbonated BDM and BW. This corresponds to an approximately 0.35 – 0.75 cm thick ejecta deposit.

In summary, the Ir content of marine boundary clays may be influenced by various sedimentary and geochemical factors (*e.g*., erosion, redeposition, geochemical remobilization and weathering). The extent to which these factors operate is dependent on the particular sedimentary site and the immediate seafloor environment. Consequently, Ir may have been concentrated or diluted in the boundary clay during sedimentation and diagenesis, and thereafter. This makes ambiguous any attempt to assess the contribution of the impactor Ir to the Ir enrichment of boundary clay or to use global fluence of Ir to calculate the chondritic impactor size. The same ambiguity goes for other PGE. In addition, in order to identify chondritic elements in the boundary clay, researchers usually present their trace element data after normalizing first to Ir and then to CI chondrites. It is clear from the above considerations that this method is also rather ambiguous.

CONCLUSION

Estimates based on the integrated Ir amount show that the decarbonated Ir-rich KPB layers at Højerup and Woodside Creek appear to contain respectfully as much as 26 and 65 % of the CC matter for the average Ir content of 465 ppb CI chondrite. These percentages are most probably an overestimation due to the high Ir input from nearby marine or continental sites, which presumably increased the primary Ir values in these clays.

ИЗВОД

АНОМАЛНЕ КОНЦЕНТРАЦИЈЕ ИРИДИЈУМА У КРЕДА–ПАЛЕОГЕН ГРАНИЧНИМ СЛОЈЕВИМА СА ЛОКАЛИТЕТА HØJERUP (STEVNS KLINT, ДАНСКА) И WOODSIDE CREEK (НОВИ ЗЕЛАНД): ПИТАЊЕ ПОРЕКЛА ВИСОКОГ УДЕЛА ХОНДРИТСКЕ КОМПОНЕНТЕ

ПАВЛЕ И. ПРЕМОВИЋ[1], БУДИМИР С. ИЛИЋ[2] и МИЛОШ Г. ЂОРЂЕВИЋ[1]

[1]*Лабораторија за геохемију, космохемију и астрохемију, Универзитет у Нишу, п. п. 224, 18000 Ниш и* [2]*Одсек за фармацију, Медицински факултет, Универзитет у Нишу, 18000 Ниш*

Креда–палеоген граничне глине са локалитета Højerup и Woodside Creek показују значајно обогаћење иридијумом у поређењу са морским седиментима. Прорачун, заснован на интегрисаном приливу иридијума по cm^2, показује да је удео угљеничног хондрита у некарбонатним фракцијама њихових иридујумом богатим слојевима 26 (Højerup) и 65 % (Woodside Creek) за просечан садржај иридијума од 465 ppb у CI хондриту. Разлог за ове високе уделе је, вероватно, значајан унос иридијума са околних морских и копнених лежишта у наведене глине.

(Примљено 4. априла, ревидирано 8. августа 2011)

REFERENCES

1. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208** (1980) 1095
2. F. T. Kyte, *Nature* **396** (1998) 237

3. A. Shukolyukov, G. W. Lugmair, *Science* **282** (1998) 927
4. R. Frei, K. M. Frei, *Earth Planet. Sci. Lett.* **203** (2002) 691
5. G. Quitté, E. Robin, F. Capmas, S. Levasseur, R. Rocchia, J. L. Birck, C. J. Allègre, *Carbonaceous or ordinary chondrite as the impactor at the K/T boundary? Clues from Os, W and Cr isotopes*, in *Proceedings of the 34th Lunar and Planetary Science Conference*, (2003), Lunar and Planetary Institute, Houston, TX, 2003, p. 1615
6. A. Trinquier, J. L. Birck, C. J. Alegret, *Earth Planet. Sci. Lett.* **241** (2006) 780
7. A. Gelinas, D. A. Kring, L. Zurcher, J. Urrutia-Fucugauchi, O. Morton, R. J. Walker, *Meteorit. Planet. Sci*. **39** (2004) 1003
8. B. Schmitz, *Geology* **16** (1988) 1068
9. L. Christensen, S. Fregerslev, A. Simonsen, J. Thiede, *Bull. Geol. Soc. Denmark* **22** (1973) 193
10. B. Schmitz, *Geochim. Cosmochim. Acta* **49** (1985) 2361
11. W. C. Elliott, *Clays Clay Miner.* **41** (1993) 442
12. F. Surlyk, T. Damholt, M. Bjerager, *Bull. Geol. Soc. Denmark* **54** (2006) 1
13. P. I. Premović, *Geochem. Int.* **47** (2009) 513
14. F. T. Kyte, J. Smit, J. T. Wasson, *Earth Planet. Sci. Lett.* **73** (1985) 183
15. R. A. F. Grieve, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **132** (1997) 5
16. T. Osawa, Y. Hatsukawa, K. Nagao, M. Koizumi, M. Oshima, Y. Toh, A. Kimura, K. Furutaka, *Geochem. J.* **43** (2009) 415
17. A. M. Vickery, H. J. Melosh, in *Global Catastrophes in Earth History*, B. Sharpton, P. Ward, Eds., Geological Society of America, Special Paper 247, Boulder, CO, 1990, p. 289
18. K. Lodders, B. Fegley Jr., *The Planetary Scientist's Companion*, Oxford University Press, New York City, New York, 1998, p. 371
19. F. T. Kyte, AGU Fall Meeting 2004, CA: B33C-0272
20. B. Bauluz, D. R. Peacor, W. C. Elliott, *Earth Planet. Sci. Lett.* **182** (2000) 127
21. J. Morgan, C. Lana, A. Kearsley, B. Coles, C. Belcher, S. Montanari, E. Díaz-Martínez, A. Barbosa, V. Neumann, *Earth Planet. Sci. Lett.* **251** (2006) 264
22. G. Graup, H. Palme, B. Spettle, *Trace element stratification in the Stevns Klint Cretaceous/Tertiary boundary layers*, in *Proceedings of the 23th Lunar and Planetary Science Conference*, (1992), Lunar and Planetary Institute Houston, TX, 1992, p. 446
23. T. J. Wdowiak, L. P. Armendarez, D. G. Agresti, M. L. Wade, Y. S. Wdowiak, P. Claeys, G. A. Izett, *Meteorit. Planet. Sci.* **36** (2001) 123
24. D. C. Colodner, E. A. Boyle, J. M. Edmond, J. Thomson, *Nature* **358** (1992) 402
25. B. Peucker-Ehrenbrink, R. E. Hannigan, *Geology* **28** (2000) 475
26. W. S. Wolbach, I. Gilmour, E. Anders, C. J. Orth, R. R. Brooks, *Nature* **334** (1988) 665
27. C. J. Hollis, C. P. Strong, K. A. Rodgers, K. M. Rodgers, *New Zeal. J. Geol. Geophys.* **46** (2003) 177
28. C. P. Strong, *New Zeal. J. Geol. Geop.* **20** (1977) 687
29. R. J. Walker, *Chem. Erde-Geochem.* **69** (2009) 101
30. A. D. Anbar, K. J. Zahnle, G. L. Arnold, S. J. Mojzsis, *J. Geophys. Res.* **106** (2001) 3219
31. E. D. Goldberg, V. Hodge, P. Kay, M. Stallard, M. Koide, *Appl. Geochem.* **1** (1986) 227.