

Asteroid breakup linked to Great Ordovician Biodiversification Event

Birger Schmitz^{1*}, David A.T. Harper², Bernhard Peucker-Ehrenbrink³, Svend Stouge², Carl Alwmark¹, Anders Cronholm¹, Stig M. Bergström⁴, Mario Tassinari¹ and Wang Xiaofeng⁵

*e-mail: birger.schmitz@geol.lu.se

The rise and diversification of shelled invertebrate life in the early Phanerozoic took place in two major steps. During the Cambrian Explosion at ca. 540 Ma a large number of new phyla appeared over a short time interval. Biodiversity at the family, genus and species level, however, remained low until the Great Ordovician Biodiversification Event (GOBE) in the mid-Ordovician¹⁻³. This event represents the most intense phase of species radiation during the Paleozoic and the biological component of planet's seafloors was irreversibly changed. The causes of the GOBE remain elusive mainly because of a lack of detailed data relating faunal to environmental change. Here we show that the onset of the major phase of the GOBE coincides at ca. 470 Ma with the disruption in the asteroid belt of the L chondrite parent body, the largest documented asteroid breakup event during the last few billion years⁴⁻⁶. The precise coincidence between an event in space and on Earth is established by bed-by-bed records of extraterrestrial chromite, osmium isotopes and invertebrate fossils in mid-Ordovician strata in Baltoscandia and China. We argue that frequent impacts on Earth of kilometer-sized asteroids accelerated the biodiversification. This is

¹ Department of Geology, University of Lund, Sölvegatan 12, SE-22362 Lund, Sweden. ² Natural History Museum of Denmark, Geological Museum, University of Copenhagen, Øster Voldgade 5-7, DK-1350 Copenhagen K, Denmark. ³ Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MS 25, Woods Hole, MA 02543, USA. ⁴ School of Earth Sciences, The Ohio State University, 125 South Oval Mall, Columbus, OH 43210, USA. ⁵ Yichang Institute of Geology and Mineral Resources, Yichang, Hubei 443003, China.

supported also by abundant mid-Ordovician fossil meteorites and impact craters⁷.

Evidence for an early Paleozoic major asteroid breakup was already established in the 1960s when recent ordinary chondrites of the L type were shown to have commonly K-Ar gas retention or shock ages of ca. 450 to 500 Ma⁴⁻⁶. About 20% of the meteorites reaching Earth today are shocked L chondrites from this event. The finds of more than 50 fossil L chondritic meteorites (1 to 20 cm in diameter) in Middle Ordovician limestone in southern Sweden show that the meteorite flux was enhanced by one to two orders of magnitude for at least a few million years after the disruption event^{7,8}. The L chondritic origin of the fossil meteorites is demonstrated by element and oxygen isotope analyses of relict chromite grains as well as by petrographic studies of chondrule textures⁷⁻⁹. Chromite is the only common mineral in chondrites that survives extensive weathering on the wet Earth surface. In the limestone beds containing common meteorites also abundant chromite grains from decomposed micrometeorites are found¹⁰⁻¹². Cosmic-ray induced ²¹Ne in chromite from the fossil meteorites increases upward in the strata, supporting a common origin from an asteroid breakup event¹³. High-precision ⁴⁰Ar-³⁹Ar dating of recent L chondrites has constrained the timing of their parent-body disruption to 470 ±6 Ma, which is identical within uncertainties to the age of 467.3 ±1.6 Ma for the beds with fossil meteorites according to the latest geologic time scale¹⁴.

During the GOBE, in the mid to late Ordovician, biodiversity at the family level increased from a Phanerozoic all-time-low in the Cambrian and early Ordovician to levels approximately three times higher in the late Ordovician^{1-3,15,16} (Fig. 1). The new biodiversity levels of marine life were matched by an increase in biocomplexity, and were sustained until the end of the Paleozoic except for short-term declines in connection with extinction events in the latest Ordovician and late Devonian. The

GOBE generated few new higher taxa, for example phyla, but witnessed a staggering increase in biodiversity at e.g. species level among a wide variety of groups of skeletal invertebrates^{2,3,16}. Diagrams of changes in global or regional biodiversity during the GOBE only give a crude representation of the timing and pace of the faunal change^{16,17}. The global signal represents a combination of many regional diversity changes across a range of fossil groups^{2,3}. The most focused global compilation through the early Paleozoic, shown in Fig. 1, demonstrates a sharp rise in biodiversity at about the Arenig-Llanvirn boundary (ca. 466 Ma). This signal is evident across a number of groups, such as the brachiopods, cephalopods and echinoderms, but less clear in some members of the Cambrian fauna (trilobites) and the Modern fauna (gastropods)¹⁶. It also corresponds to the second cycle diversity peak in conodonts recognized by Sweet¹⁸. The causes of the GOBE, and its relation to both intrinsic (biological) and extrinsic (environmental) factors are not known². Many authors have suggested a link to increasing levels of atmospheric oxygen, favoring the radiation of aerobic metazoan life together with an expansion of the phyto and zooplankton^{19,20}.

Although biodiversity diagrams such as in Fig. 1 show the broad outline of change, at a higher resolution they suffer from the effects of poor correlation and poor preservation of faunas, "monographic bursts", and data binning. In order to relate biological change to physical events, detailed high-resolution, multiparameter records across complete and fossil-rich sections are required. Here we have constrained the precise stratigraphic level for the L chondrite disruption event by searches for sediment-dispersed extraterrestrial (chondritic) chromite (EC) grains and Os isotopic studies in mid-Ordovician sections with condensed limestone (Fig. 2). These results are matched by the so far most detailed bed-by-bed studies of the distribution of brachiopod species across mid-Ordovician strata in Baltoscandia (Fig. 3).

The sections studied for EC grains occur at Kinnekulle and in southern Scania, 350 km apart in southern Sweden, and at Puxi River (Puquie) and Fenxiang, 4 km apart, in south-central China near Yichang, Hubei province. The EC grains (>63 μm) have been retrieved from ca. 10-30 kg sized limestone samples that were dissolved in HCl and HF acid¹¹. The EC can be readily distinguished from terrestrial chromite by its distinct element composition^{7,11}. The results of the EC searches are shown in Fig. 2 and in the Supplementary Information. In the section studied in greatest detail, at Kinnekulle, in 379 kg of limestone from 14 levels across 9 m of strata below the *Lenodus variabilis* Zone only 5 EC grains were found¹¹ (Fig. 2). The values then increase dramatically to typically 1-3 EC grains per kg of rock in the *L. variabilis*, *Yangtzeplacognathus crassus* and *Microzarkodina hagetiana* zones. In this interval a total of 332 EC grains were found in 174 kg rock. In southern Scania and in China the distribution trends of EC grains are very similar to that at Kinnekulle. In southern Scania some beds in the *L. variabilis* Zone contain up to 6 EC grains per kg of rock, whereas only 2 grains were found in 125 kg in the beds spanning 7 m below¹². In the Chinese sections, 89 kg of limestone below the *L. variabilis* Zone yielded only one EC grain compared to 117 EC grains in 89 kg in the overlying beds (Fig. 2).

The first appearance of common EC grains in the lower *L. variabilis* Zone in the three sections is a strong indication of the precise timing of the disruption of the L chondrite parent body. The data also represent strong support for an increase by two orders of magnitude in the flux of micrometeorites to Earth following the disruption event, as previously suggested based on studies of the Swedish sections alone¹⁰⁻¹². There is no indication that changes in sedimentation rates, on average a few millimeter per thousand years, can explain the observed major trend in EC concentrations, although individual beds may have formed at different rates. That the disruption event

occurred in the lower *L. variabilis* Zone is consistent with cosmic-ray induced ^{21}Ne ages of chromite grains from the fossil meteorites¹³. In 5-10 million years younger condensed limestone in the Gärde quarry, central Sweden, we found 9 EC grains in 23 kg of rock. This indicates that the EC flux is still enhanced compared to that before the asteroid breakup. The low pre-breakup concentrations of EC grains are similar to concentrations measured in similarly condensed sediments from much younger periods. For example, in 210 kg of pelagic limestone (average sedimentation rate ca. 2.5 mm kyr^{-1}) from the famous late Cretaceous-Paleocene Gubbio section in Italy we only found 6 EC grains²¹.

The results from our analyses of $^{187}\text{Os}/^{188}\text{Os}$ in whole-rock limestone samples through the Kinnekulle section show a relatively stable trend with ratios around 0.6-0.8 through the lower 11 m of section, but from the same bed where the EC grains become common and upwards, ratios mainly lie in the range 0.3-0.5 (Fig. 2; Supplementary Information). The simplest explanation for this prominent change is an increasing influence of an extraterrestrial component ($^{187}\text{Os}/^{188}\text{Os} \sim 0.12$) at the expense of a detrital/hydrogenous Os component ($^{187}\text{Os}/^{188}\text{Os} \sim 0.8$)²², well in line with conclusions based on EC trends.

Some of the best sections for studies of Ordovician invertebrate diversification occur in Baltoscandia²³. We have established the mid-Ordovician biodiversity trends for brachiopods based on bed-by-bed sampling of more than 30,000 fossils from eight sections in Baltoscandia (Fig. 3). The phylum Brachiopoda dominated the benthos of the Paleozoic evolutionary fauna both in abundance and diversity and formed a pivotal part of the suspension-feeding food chains of the era. The phylum was widely dispersed across shallow to deep-water environments around all the palaeocontinents. We show here that there are two intervals in the succession when the Baltoscandian

brachiopod fauna suffered dramatic changes - one within the lower part of the regional Volkhov Stage and one at the base of the Kunda Stage (Fig. 3). The largest change occurs during exactly the same interval when the L chondritic extraterrestrial flux peaks at the base of the Kunda Stage, and when brachiopods more typical of the Paleozoic evolutionary fauna, i.e. orthides and strophomenides, diversified.

Modeling studies suggest an enhanced flux of extraterrestrial matter, including large asteroids, during 10-30 million years after major asteroid disruption events²⁴. The L chondrite parent body break-up at 470 Ma is thought to have created the Flora family of asteroids²⁵. These asteroids were particularly prone to enter Earth-crossing orbits because of their position relative to an important orbital resonance^{24,25}. Apparently the mid-Ordovician interval with enhanced extraterrestrial flux is broadly coincident with the main phase of the GOBE^{1-3,16}. At least in Baltoscandia the onset of the two events appears to coincide precisely (Figs. 2-3). Albeit speculative, the best explanation for the coincidence is that frequent impacts on Earth of large asteroids, fragments of the L chondrite parent body, generated changes in the biota. Impact related environmental perturbations may have accelerated a process driven also by intrinsic biological mechanisms. Although much contemporary research has focused on the negative effects of large impacts, such as in the Cretaceous-Tertiary boundary case²⁶, more minor and persistent impacts could generate diversity by creating a range of new niches across a mosaic of more heterogeneous environments. Such diversity increases are predicted by the well-established Intermediate Disturbance Hypothesis, initially applied to diversity changes in coral reefs and tropical rain forests²⁷. Frequent impacts may also have destabilized ecological communities, allowing invasive species to take over and displace incumbent communities. The ecological and taxonomic amplitudes of the mid-Ordovician biodiversification may be decoupled and there are important

feedback loops in the process. This phase of the diversification is marked by a brachiopod takeover from trilobites in benthic communities, and the establishment of recumbent life modes and size increases in many brachiopod clades. However, in contrast to the carnivores and detritus feeders of the Modern fauna, the Paleozoic fauna was now dominated by a suspension-feeding benthos with low metabolic rates better equipped to deal with and benefit from major environmental disruptions.

There are about 170 known impact craters on Earth and their record shows that impacts may have been more common by a factor of 5-10 during the mid-Ordovician compared to other periods of the Phanerozoic^{7,14}. Four of seventeen known impact craters in Baltoscandia (Granby, Lockne, Kärddla, and Tvären craters) are of Middle to early Late Ordovician age. For only very few of Earth's craters has it been possible to determine the impactor type, but for at least the Lockne crater (458 Ma) in central Sweden chromite in resurge deposits has implicated an L chondritic impactor²⁸.

The strata in China and Baltoscandia that we show are rich in fossil meteorites and/or EC grains have long been known to include horizons with unusual lithologies. Over several hundred thousand square kilometers in southern Sweden the succession of homogeneous red orthoceratite limestone is interrupted by a one-meter thick anomalous grey, clay-rich interval with a peculiar fauna. During deposition of this bed cm-sized cystoids appear to have literally covered the sea floor of a major part of the Baltic Basin. In west Russia peculiar ooid-horizons characterize the interval, and in China unusual mini-mounds interrupt the normal succession of nodular marl and limestone²⁹ (Fig. 2). The possible relationship of these anomalous lithologies and structures to asteroid impacts or other astronomical perturbations, like solar system gravity disturbances, certainly warrants further studies. As shown here, at least on a regional scale, there is a close temporal coincidence between major biological change

and the disruption of the L chondrite parent body.

Recently the impactor at the Cretaceous-Tertiary boundary has been tied by modeling to an asteroid disruption event at 160 Ma³⁰, but this event may not have led to a pronounced asteroid shower as focused in time as the one in the mid-Ordovician, and it has not left any obvious signal in the collision history of present-day meteorites.

METHODS

For chromite searches, samples of typically 10-30 kg of limestone were crushed and decalcified first in 6 M HCl and then in 18 M HF at room temperature. The acid-insoluble fraction, 63-355 μm , was searched for opaque minerals under the binocular microscope. Picked grains were mounted in epoxy resin and polished to a flat surface using 1 μm diamond slurry. Element analyses were performed with SEM-EDS^{10-12,28}. The EC grains are characterized in the first hand by high Cr₂O₃ contents of ~55-60 wt%, FeO concentrations in the range of ~25-30 wt%, low Al₂O₃ at ~5-8 wt%, and MgO concentrations of ~1.5-4 wt%. The most discriminative feature, however, is narrow ranges of V₂O₃, ~0.6-0.9 wt%, and TiO₂, ~2.0-3.5 wt%, concentrations. For a grain to be classified as an EC grain, it has to have a composition within the defined ranges for all elements listed¹¹.

For Os analyses whole-rock limestone samples were ground in an agate mortar. Between 3-10 gram of powdered sediment was weighted, mixed with an isotopically enriched spike containing ¹⁹⁰Os, dried at room temperature over night and then mixed with borax, nickel and sulfur powder. After fusing the mixture for 90 minutes at 1000°C the NiS bead was separated and dissolved in 6.2 M HCl and the residue filtered at 0.45 μm . Insoluble PGE-containing particles were dissolved in concentrated HNO₃ in a tightly closed Teflon vial at ~100°C. After dissolution the Teflon vial was

chilled in ice water to minimize the escape of volatile OsO₄. Osmium was then extracted from this vial with the sparging method directly into the torch of a single-collector ICPMS (Finnigan Element). Typical Os blanks are < 1 pg/g. Depending on the Os concentration the precision in ¹⁸⁷Os/¹⁸⁸Os is between 0.5% and a few percent. The details of the method and an evaluation of the accuracy and precision of the data have been published elsewhere³¹.

References

1. Sepkoski Jr., J. J. A factor analytic description of the Phanerozoic marine fossil record. *Paleobiology* **7**, 36-53 (1981).
2. Webby, B. D., Paris, F., Droser, M. L. & Percival, I. G. Eds., *The Great Ordovician Biodiversification Event* (Columbia University Press, New York, 2004).
3. Harper, D. A. T. The Ordovician biodiversification: Setting an agenda for marine life. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **232**, 148-166 (2006).
4. Heymann, D. On the origin of hypersthene chondrites: Ages and shock effects of black chondrites. *Icarus* **6**, 189-221 (1967).
5. Keil, K., Haack, H. & Scott, E. R. D. Catastrophic fragmentation of asteroids: evidence from meteorites. *Planet. Space Sci.* **42**, 1109-1122 (1994).
6. Kunz, J., Falter, M. & Jessberger, E. K. Shocked meteorites: Argon-40-argon-39 evidence for multiple impacts. *Meteorit. Planet. Sci.* **32**, 647-670 (1997).
7. Schmitz, B., Tassinari, M. & Peucker-Ehrenbrink, B. A rain of ordinary chondritic meteorites in the early Ordovician. *Earth Planet. Sci. Lett.* **194**, 1-15 (2001).
8. Bridges, J. C. *et al.* Petrographic classification of mid-Ordovician fossil meteorites from Sweden. *Meteorit. Planet. Sci.* (in press) (2007).
9. Greenwood, R. C., Schmitz, B., Bridges, J., Hutchison, R. & Franchi, I. A.

Disruption of the L chondrite parent body. New oxygen isotope evidence from Ordovician relict chromite grains. *Earth Planet. Sci. Lett.* (in press) (2007).

10. Schmitz, B., Häggström, T. & Tassinari, M. Sediment-dispersed extraterrestrial chromite traces a major asteroid disruption event. *Science* **300**, 961-964 (2003).

11. Schmitz, B. & Häggström, T. Extraterrestrial chromite in Middle Ordovician marine limestone at Kinnekulle, southern Sweden - Traces of a major asteroid breakup event. *Meteorit. Planet. Sci.* **41**, 455-466 (2006).

12. Häggström, T. & Schmitz, B. Distribution of extraterrestrial chromite in Middle Ordovician Komstad Limestone in the Killeröd quarry, Scania, Sweden. *Bull. Geol. Soc. Den.* **55**, 37-58 (2007).

13. Heck, P. R., Schmitz, B., Baur, H., Halliday, A. N. & Wieler, R. Fast delivery of meteorites to Earth after a major asteroid collision. *Nature* **430**, 323-325 (2004).

14. Korochantseva, E. V. *et al.* L-chondrite asteroid breakup tied to Ordovician meteorite shower by multiple isochron ^{40}Ar - ^{39}Ar dating. *Meteorit. Planet. Sci.* **42**, 113-130 (2007).

15. Droser, M. L. & Sheehan, P. M. Palaeoecology of the Ordovician radiation; resolution of large-scale patterns with individual clade histories, palaeogeography and environments. *Geobios* **30** (suppl. 1), 221-229 (1997).

16. Sepkoski Jr., J. J. in *Ordovician Odyssey: Short Papers for the Seventh International Symposium on the Ordovician System* (Eds. Cooper, J. D., Droser, M. L. & Finney, S. C.) (Pacific Section Society for Sedimentary Geology, Book 77, Fullerton, CA, 1995).

17. Hammer, Ø. Biodiversity curves for the Ordovician of Baltoscandia. *Lethaia* **36**, 305-314 (2003).

18. Sweet, W. C. *The Conodonts. Morphology, Taxonomy, Palaeoecology, and Evolutionary History of a long-extinct animal Phylum*. Clarendon Press, Oxford, (1988).
19. Peterson, K. J. Macroevolutionary interplay between planktic larvae and benthic predators. *Geology* **33**, 929-932 (2005).
20. Vecoli, M., Lehnert, O. & Servais, T. The role of marine microphytoplankton in the Ordovician Biodiversification Event. *Notebooks on Geology, Memoir* **2005/02**, 69-70 (2005).
21. Cronholm, A. & Schmitz, B. Extraterrestrial chromite in latest Maastrichtian and Paleocene pelagic limestone at Gubbio, Italy: The flux of unmelted ordinary chondrites. *Meteorit. Planet. Sci.* (in press).
22. Peucker-Ehrenbrink, B. & Ravizza, G. The marine osmium isotope record. *Terra Nova* **12**, 205-219 (2000).
23. Rasmussen, C. M. Ø., Hansen, J. & Harper, D. A. T. Baltica: A mid Ordovician diversity hotspot. *Hist. Biol.* **19**, 255-261 (2007).
24. Zappalà, V., Cellino, A., Gladman, B. J., Manley, S. & Migliorini, F. Asteroid showers on Earth after family breakup events. *Icarus* **134**, 176-179 (1998).
25. Nesvornyy, D., Vokrouhlicky, D., Bottke, W.F., Gladman, B. & Häggström T. Express delivery of fossil meteorites from the inner asteroid belt to Sweden. *Icarus* **188**, 400-413 (2007).
26. Alvarez, L. W., Alvarez, W., Asaro, F. & Michel, H. V. Extraterrestrial cause for the Cretaceous-Tertiary extinction. *Science* **208**, 1095-1108 (1980).
27. Connell, J.H. Diversity in tropical rain forests and coral reefs. *Science* **199**, 1302-1310 (1978).
28. Alwmark, C. & Schmitz, B. Extraterrestrial chromite in the resurge deposits of the

early Late Ordovician Lockne crater, central Sweden. *Earth Planet. Sci. Lett.* **253**, 291-303 (2007).

29. Zhang, J. *Middle Ordovician conodonts from the Atlantic Faunal Region and the evolution of key conodont genera*. Thesis, Univ. Stockholm (1998).

30. Bottke W. F., Vokrouhlicky, D. & Nesvorný, D. An asteroid breakup 160 Myr ago as the probable source of the K/T impactor. *Nature* **449**, 48-53 (2007).

31. Peucker-Ehrenbrink, B., Bach, W., Hart, S.R., Blusztajn, J. S. & Abbruzzese, T. Rhenium-osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. *Geochem. Geophys. Geosyst.* **4**, art. no. 8911 (2003).

Author information Correspondence and requests for material should be addressed to B.S. The authors declare no competing financial interests.

Acknowledgements This study was supported by funds to B.S. from the National Geographic Society, Swedish Research Council (VR) and Crafoord Foundation and to D.A.T.H. from the Carlsberg Foundation.

Figure captions

Figure 1. Global biodiversity change at family level through the early Paleozoic.

Although this diagram from Sepkoski (1995)¹⁶ gives a good representation of the overall biodiversity trend, the resolution is too crude for correlation with field data.

Figure 2. Distribution of extraterrestrial (chondritic) chromite and osmium isotopes through Middle Ordovician sections in Sweden and China. Results are

shown for sections at Kinnekulle (Hällekis and Thorsberg quarries) and southern Scania (Killeröd and Fågelsång sections), 350 km apart in southern Sweden, and the Puxi River and Fenxiang sections, 4 km apart in south-central China. Shown also is the distribution of Os isotopes across the Hällekis section. The stratigraphic interval yielding abundant fossil meteorites in the Thorsberg quarry is indicated⁷. The conodont biostratigraphy shown has been produced specifically for this study, using consistent taxonomic concepts for the different sections.

Figure 3. Total diversity of brachiopod species (number of species) through part of the Lower and Middle Ordovician in Baltoscandia. The results are based on bed-by-bed collections at eight localities²³. Note the dramatic increase in biodiversity (black line) and high extinction (blue line) and origination (red line) levels following the regional Volkhov-Kunda boundary, i.e. the same level where extraterrestrial chromite appears and Os isotopes change in Fig. 2.

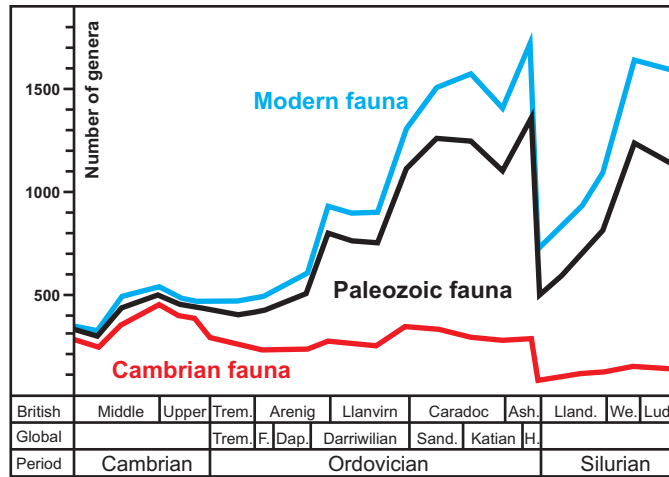


Fig. 1

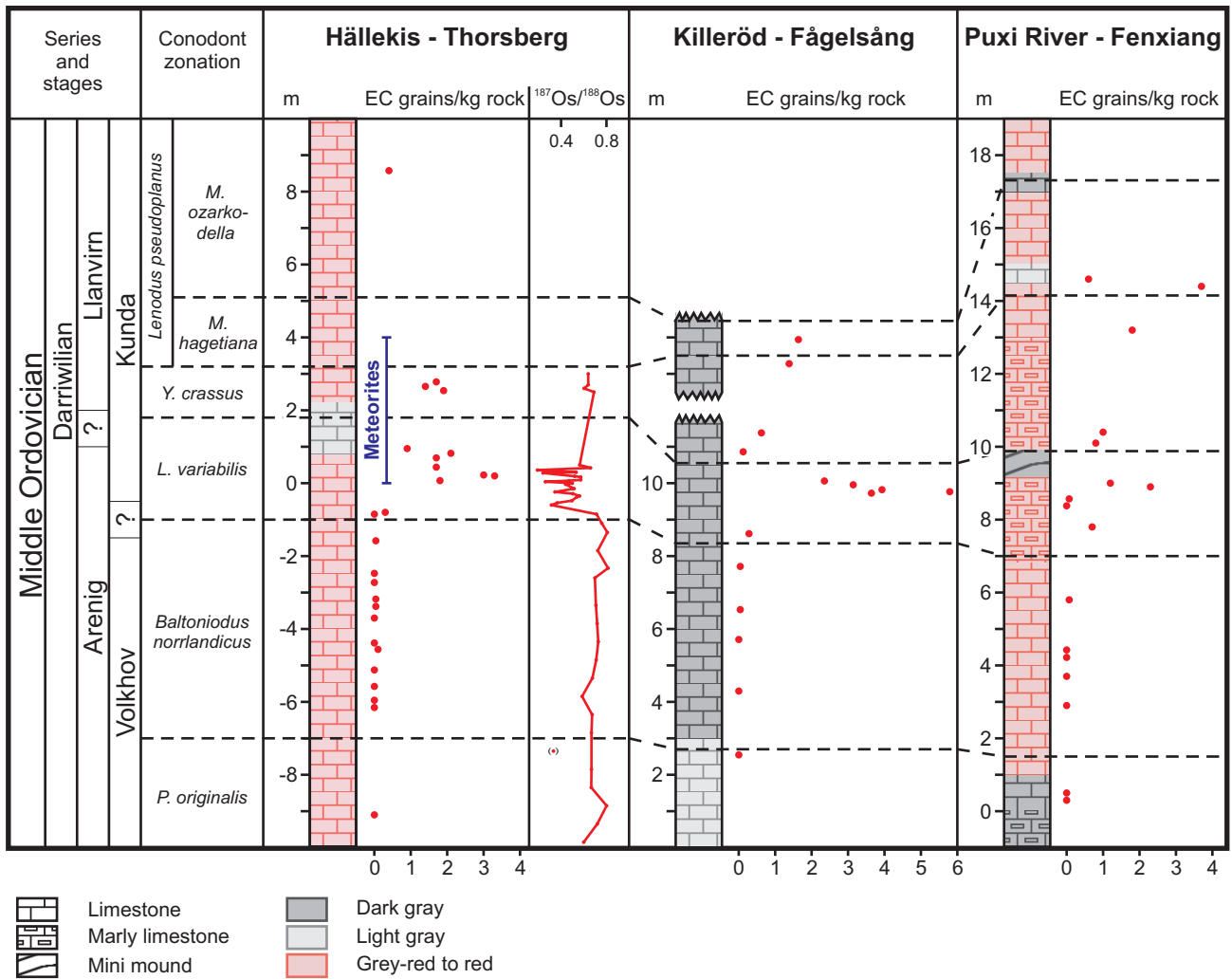


Fig. 2

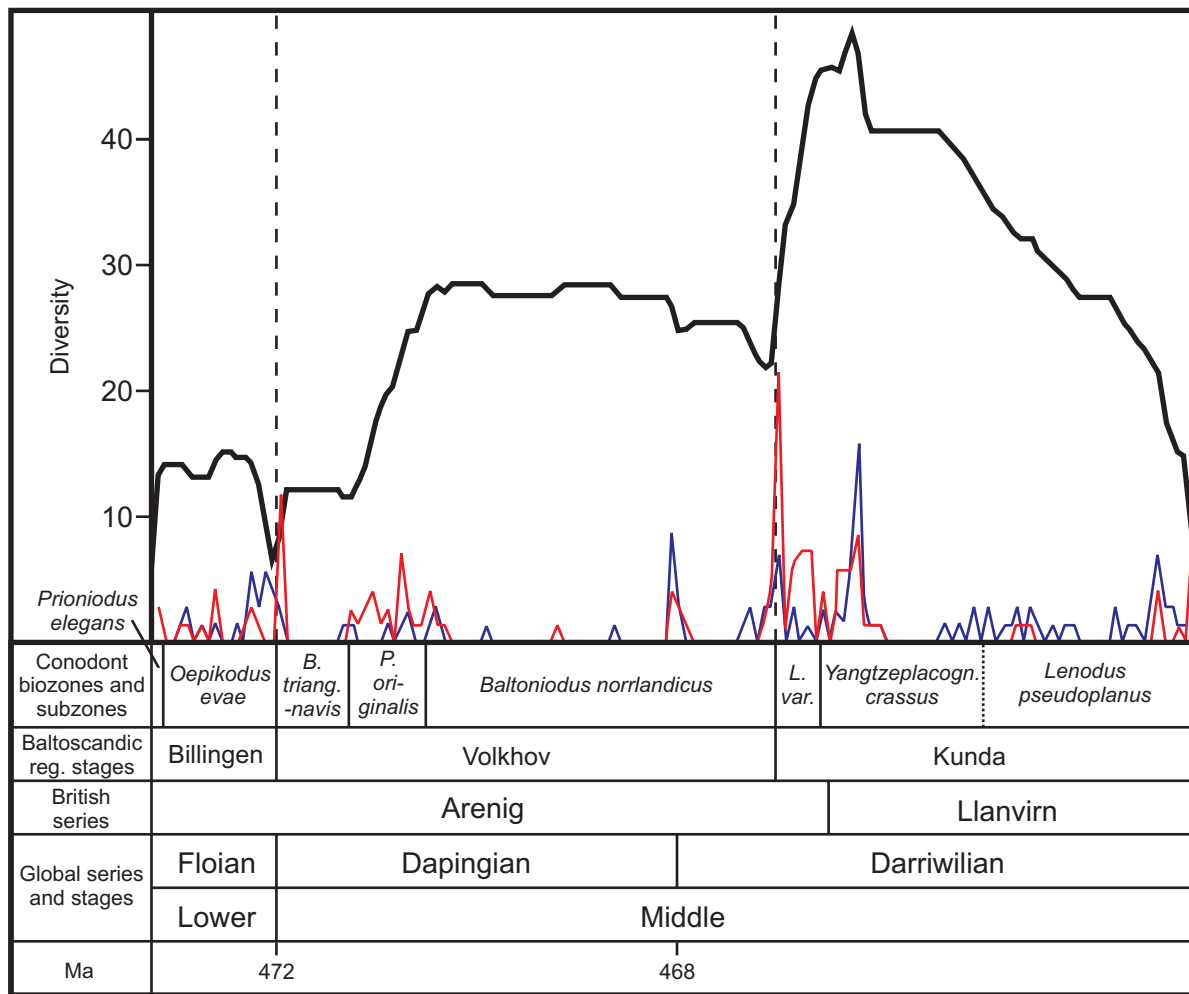


Fig. 3