Metal-induced malformations in early Palaeozoic plankton are harbingers of mass extinction

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Glacial episodes have been linked to Ordovician–Silurian extinction events, but cooling itself may not be solely responsible for these extinctions. Teratological (malformed) assemblages of fossil plankton that correlate precisely with the extinction events can help identify alternate drivers of extinction. Here we show that metal poisoning may have caused these aberrant morphologies during a late Silurian (Pridoli) event. Malformations coincide with a dramatic increase of metals (Fe, Mo, Pb, Mn and As) in the fossils and their host rocks. Metallic toxins are known to cause a teratological response in modern organisms, which is now routinely used as a proxy to assess oceanic metal contamination. Similarly, our study identifies metal-induced teratology as a deep-time, palaeobiological monitor of palaeo-ocean chemistry. The redox-sensitive character of enriched metals supports emerging ‘oceanic anoxic event’ models. Our data suggest that spreading anoxia and redox cycling of harmful metals was a contributing kill mechanism during these devastating Ordovician–Silurian palaeobiological events.
Orдовик–Силурские отложения отражают несколько драматических, положительных и устойчивых изотопных экскурсий, указывающих на серьезные нарушения окружающей среды, океана, кислорода и сульфатных циклов. Изменения окружающей среды, связанные с этими нарушениями, оказали поистине катастрофический эффект на жизнь. Одни из этих событий (конец-ордовикские–хирнантские) включают в себя “Большой пять” массовые вымирания палеозойского периода. Другие аналогичные события также отражают существенно повышенные уровни вымирания, включая потери трилобитов, брахиопод и кораллов, а также ордовик–силурские события. Эти массовые вымирания обычно сопровождаются значительным изменением окружающей среды, включая снижение уровня морского кислорода, трофических изменений и геохимических смещений. Эти изменения являются серьезными, поскольку они могут привести к многочисленным нарушениям в окружающей среде.

Результаты
Читиноозан тератология. Малоправильные акритархи (глины и протозоны) могут быть обильны в глубоководных сообществах в различные эпохи. Например, в раннем палеозое, когда эти сообщества были наиболее обильными, можно было обнаружить значительные количества читиноозанов. Если эти сообщества были обильны, то можно было бы ожидать, что они также представлены в глиняных образцах, которые были взяты из различных интервалов.

Мы выбрали средний придолийский (поздний силур) для изучения одного из событий с повышенным уровнем тератологии. Мы исследовали геохимические сигналы читиноозанов в одном из событий, где повышенные уровни тератологии соответствовали металлической загрязненности палеозойских образований. Мы также исследовали геохимические сигналы читиноозанов в других событиях, где повышенные уровни тератологии соответствовали металлической загрязненности палеозойских образований. Мы использовали новые комбинации методов для измерения металлического содержания в индивидуальных палynomорфах и тератологии, которые помогут нам лучше понять, как эти нарушения влияли на окружающую среду в прошлом.

Изображение 1 | Тератологические и нормальные читиноозаны из шурфа 14 в А1-61 резервуаре. (a) Тератологический образец Ancyrochitina (образец 2,127,5 м). (b) Морфологически нормальный образец Ancyrochitina для сравнения (образец 2,127,5 м). (c) Сетка из трех образцов Ancyrochitina, с нормальным образцом в пределах двух нормальных образцов (образец 2,126,75 м). Масштабные линии, 100 мкм. стрелки указывают на аномальное развитие.
Geochemistry. The metal content, particularly Fe, Cu, As, Al, Pb, Ba, Mo and Mn, of individual chitinozoans and/or bulk-rock samples increases markedly in the teratological interval (Fig. 3a). Fe, As and Mn concentrations in bulk-rock samples increase by an order of magnitude, for example, from c. 50,000 to c. 400,000 p.p.m. Fe, on cue with the appearance of oolitic-ferruginous beds in the stratigraphic section (Fig. 3b). Principal component analysis on the ToF-SIMS data clearly separates the lower samples from those of the teratological interval; this is due to elevated metal content of the chitinozoan specimens in assemblages with malformation, notably of Fe, Al, Mo and Ba (Fig. 4a). While the metal enrichment in the teratological horizon is evident both in individual chitinozoans and in bulk-rock chemistry, abundances of certain elements in bulk-rock samples are decoupled from those in the palynomorphs: for example, bulk-rock Ba contents are relatively constant, yet the chitinozoan Ba shows a significant increase in the teratological zone (Fig. 3a). In addition, at decimetre scale and notably within the horizon with malformations, specimen and bulk-rock chemistry is statistically decoupled for all elements as evidenced by time-series cross-correlation tests (Figs 3b and 4b). This decoupling demonstrates that the chemistry of chitinozoans is not a mere imprint of rock composition but may preserve the original chemistry of the organisms and thus reflect metal abundances in their aquatic environment. Relying exclusively on the chemical signature of the chitinozoans to represent original ocean chemistry may be subject to debate. However, the coincidence between malformations, a primary biological feature developed in vivo, and the increased metal contents in the organisms and sediments, in combination, is best explained by an increase in dissolved metals in the water column during the life of the organism and deposition of the sediments. We conclude that metal pollution, that is, the uptake of those metals during life and/or harmful conditions that developed in tandem with a rising metal content of the seawater, is the most likely explanation for the increase of teratology observed in these fossils.

Discussion

The mid-Pridoli teratology event correlates with faunal turnover and a positive δ13C excursion (Fig. 5). Early Palaeozoic bioevents were generally accompanied by large, positive δ13C excursion. Consensus is converging that such signatures may reflect the burial and sequestration of isotopically light carbon on the deep seafloor during developing OAEs. It is also well established that transitions to anoxic conditions in modern marine environments increase markedly the solubility of some metals in seawater. Most significantly, suboxic conditions lead to the reductive dissolution of Fe–Mn oxyhydroxides, increasing the concentration of Fe and Mn in modern seawater by orders of magnitude. The concentration of some trace elements such as As, Mo and rare earth elements are directly controlled by absorptive scavenging and co-deposition with these oxyhydroxides; and as a consequence of reductive dissolution of oxyhydroxides, increase significantly in concentration in the seawater. Moreover, transitions from oxic to anoxic oceanic conditions can trigger massive shifts in the cycling of Fe–Mn oxyhydroxides sequestered in sub-seafloor sediments, thereby triggering a benthic flux of Fe, Mn and associated trace elements from the sediments into the anoxic seawater. Other elements, such as Ba, are governed by linked processes such as the reduction of sulfate in anoxic seawater. It is also well established that transitions to anoxic conditions in modern marine environments increase markedly. The metal content, particularly Fe, Cu, As, Al, Pb, Ba, Mo and Mn, of individual chitinozoans and/or bulk-rock samples increases markedly in the teratological interval (Fig. 3a). Fe, As and Mn concentrations in bulk-rock samples increase by an order of magnitude, for example, from c. 50,000 to c. 400,000 p.p.m. Fe, on cue with the appearance of oolitic-ferruginous beds in the stratigraphic section (Fig. 3b). Principal component analysis on the ToF-SIMS data clearly separates the lower samples from those of the teratological interval; this is due to elevated metal content of the chitinozoan specimens in assemblages with malformation, notably of Fe, Al, Mo and Ba (Fig. 4a). While the metal enrichment in the teratological horizon is evident both in individual chitinozoans and in bulk-rock chemistry, abundances of certain elements in bulk-rock samples are decoupled from those in the palynomorphs: for example, bulk-rock Ba contents are relatively constant, yet the chitinozoan Ba shows a significant increase in the teratological zone (Fig. 3a). In addition, at decimetre scale and notably within the horizon with malformations, specimen and bulk-rock chemistry is statistically decoupled for all elements as evidenced by time-series cross-correlation tests (Figs 3b and 4b). This decoupling demonstrates that the chemistry of chitinozoans is not a mere imprint of rock composition but may preserve the original chemistry of the organisms and thus reflect metal abundances in their aquatic environment. Relying exclusively on the chemical signature of the chitinozoans to represent original ocean chemistry may be subject to debate. However, the coincidence between malformations, a primary biological feature developed in vivo, and the increased metal contents in the organisms and sediments, in combination, is best explained by an increase in dissolved metals in the water column during the life of the organism and deposition of the sediments. We conclude that metal pollution, that is, the uptake of those metals during life and/or harmful conditions that developed in tandem with a rising metal content of the seawater, is the most likely explanation for the increase of teratology observed in these fossils.

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Consequently, the metals were re-oxidized and precipitated, each at their own pace (Supplementary Dataset 1), at the redox interface between the anoxic water mass and local oxic surface waters. This scenario accounts for the accumulation of redox-sensitive metals in both the sediments and fossils and explains the teratology of organisms during the Pridoli event. This interpretation is supported by similar enrichments of redox-sensitive metals through the early Wenlock Ireviken event 12, by the enrichment of rare earth elements in widespread phosphorites across Laurentia 42, and by the concurrence of ironstones with Silurian C-isotope excursions in the Appalachian Basin (USA). The US sections display consistent patterns of red, green and black marine sedimentary rocks, indicative of increasingly anoxic conditions10. In this model, the harmful effects of spreading dead zones43, decreasing oxygen and increasing metal concentrations are intricately entangled. For instance, a study44 of the seasonally anoxic Chesapeake Bay links the sudden occurrence of malformed foraminifer Ammonia to the onset of anoxic conditions in the 1970s. However, it is also known that these seasonal anoxic conditions triggered the prompt release of redox-sensitive metals from the sediments into the water column 40. In our Silurian data, metal-enriched malformed assemblages occur at the onset of the carbon isotope excursions, while hypoxia was starting to spread (and before it peaks later, indicated by the deposition of black shales 10). This suggests that a direct toxic effect of metal enrichment contributed to the most plausible mechanism for the deformities in the organisms. Other environmental stressors that are known to cause malformation in the modern include changes in light intensity, ultraviolet radiation, predation, salinity and pH, and could have coincided with spreading anoxic waters, but there is no empirical evidence for such changes in the event interval.

Figure 3 | Geochemical signal of selected elements through well A1-61. (a) Whole-rock Fe, Mn and As data display clear peaks in the chitinozoan teratological interval, markedly above background values lower in the well (LA-ICP-MS, in p.p.m.). Analyses on individual chitinozoans exhibit peaks in certain elements (Fe and Ba) in the teratological interval (ToF-SIMS, semi-quantitative). Asterisks (*) indicate saturation at detector (that is, underestimated values). Elements (for example, As and Mn) subject to spectral interference and/or below detection limit of the ToF-SIMS analyses cannot be directly compared with the bulk rock. (b) Geochemical signals in the event horizon. Concentrations of whole-rock Fe, Mn, and As data, as well as Fe and Ba in individual chitinozoans are significantly above background. Green arrows mark samples with teratological chitinozoans.
of the Earth’s atmosphere and hydrosphere. Yet, generally, uncertainty remains regarding the primary metal abundances in seawater, pathways of metal accumulation and post-depositional modification of metal abundances in sedimentary rocks. As demonstrated in modern marine environments, our results suggest that metal-induced teratology of fossil plankton may serve as an independent proxy for monitoring changes in the metal concentrations of the shallow palaeo-ocean. This new proxy enables us here to reduce these uncertainties and supports the interpretation that the sedimentary chemistry reflects changing oceanic metal compositions during OAEs. As such, this proxy has the potential to help unravel the complexities inherent to sedimentary geochemistry, and may be a tool to evaluate other instances of marine metal variation through the geological record.

The co-occurrence between mid-Pridoli teratology and the onset of extinction suggests that metal contamination may have played a direct role in the biological crisis at large. More generally, the recurring temporal match between Ordovician–Silurian teratology events and extinction events raises the prospect that toxic metal contamination may be a previously unrecognized contributing agent to many, if not all, of these bioevents (Fig. 5).

In sections where such data exist, teratological phytoplankton precede or co-occur with the earliest phases of these major extinction events. Taken at face value, for example, Hirnantian acritarch malformation in the Lousy Cove Member (member 6) of the Ellis Bay Formation coincides with the onset of the ‘phytoplankton crisis’ on Anticosti Island (Canada) but precedes the major macrofauna extinctions in the overlying Laframboise

Figure 4 | Statistical analyses of the geochemical data. (a) Principal component analysis (PCA) of ToF-SIMS data of chitinozoans indicates a clear separation of samples from within (green stars) and outside (red triangles) of their teratological interval, based on their geochemistry and mainly driven by elements such as Fe, Al, Cu, Ba, Mo and Pb. The PCA was carried out using the Eigenvector PLS toolbox (Eigenvector Research Inc., Wenatchee, WA, USA) in the MATLAB environment version 8.0 (The MathWorks, Natick, MA, USA). Data on 19 elements of 141 ToF-SIMS spectra (spread over 13 stratigraphical levels) were pre-scaled using auto-scaling (spectral variables are scaled to a zero mean and unit variance) as some of the spectral peaks of interest are relatively small. Three samples were extremely enriched in Fe and Al and these outliers were eliminated. (b) Correlation values between element concentrations in chitinozoans and whole-rock data. Measurements were averaged across 20-cm intervals of core and scaled to a mean of zero and unit variance before non-parametric correlation tests. Red lines indicate approximate correlation coefficients for a significant cross-correlation ($P = 0.05$). Only Ti is significantly correlated between chitinozoans and rock samples. PC, principal component.

Figure 5 | Distribution of potential OAEs in the uppermost Ordovician and Silurian. The position of the suggested OAEs is based on $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy. Key victims of the extinction events and the events with increased occurrences of teratology are highlighted. Metal toxicity is observed in the Pridoli (this study) and implied during the Ireviken event, where metal enrichments in carbonates and phosphates in SE Sweden indicate anoxia. For a full list of affected fauna see Kaljo et al. and Calner. Ord., Ordovician; Dev., Devonian.
Member (member 7) (refs 14,45). On Gotland (Sweden), increased acritarch malformation occurs around a series of marker beds, identifying an interval that starts below the strongest extinctions of conodonts during the early Ireviken event. Although the patterns and exact relative timing of strongest extinctions of conodonts during the early Ireviken iron oolite bed in core 14 was sampled systematically, as oolites do not normally intervals. The original biostratigraphic purpose of the well explains why not every in Libya that cuts through the Mesozoic, Devonian, Silurian and into the Upper Palaeozoic extinctions.

Metal toxicity, and its fossilized in vivo expressions, could provide the ‘missing link’ between extinction of faunas on the shelf, and widespread ocean anoxia. As part of a series of complex systemic interactions accompanying these shifts in ocean conditions, the redox cycling of metals may identify the early phase of the kill mechanisms that culminated in these catastrophic events. Although OAEs typically entail rapid climatic change, our data suggest that the proposed mechanisms of these early palaeozoic mass extinctions were previously too simply linked to global cooling, invoking thermal stress and habitat reduction. Ultimately, metal-induced teratology might become a new forensic tool to identify palaeoenvironmental signatures and may help unravel the biogeochemical and systematics that define these extraordinary periods of Earth history.

Methods

Material. Samples were studied from the 3,176 m A1-61 borehole in Mal-el-Dorah in Libya that cuts through the Mesozoic, Devonian, Silurian and into the Upper Ordovician sequence. The samples were collected from infrequently cored Silurian intervals. The original biostratigraphic purpose of the well explains why not every iron ore olite bed in core 14 was sampled systematically, as oolites do not normally yield age-diagnostic microfossils (Fig. 2). Our samples 2,127 and 2,125 are direct subsamples from those of Jaglin and Paris. Note that the palaeontological interval for chitinozoans in core 14 has been extended downwards by 0.5 m (Fig. 2) compared with published range as we found additional malformed specimens at 2,127.5 m (Supplementary Dataset 1).

Palynology. Thirty samples from A1-61 were dissolved for palynology. The core chips were broken into 0.5-cm pieces and decarbonated using 34% HCl. They were then digested with c. 200 ml 48% HF over c. 24 h. Any newly formed fluor silicates were removed using a second 17% HCl treatment, over 32 h and at 60 °C. Samples were neutralized and filtered at 51 μm. Individual palynomorphs were handpicked from the organic residue (>51 μm) using a stereomicroscope at >50-150 magnification, and transferred onto glass slides with Cu-tape and microscope grids, which were then used in TOF-SIMS analyses. Scanning electron microscope positioning of specimens versus reference grid was used to identify the specimens in the TOF-SIMS.

Time-of-flight secondary ion mass spectrometry. Individual microfossils from 13 samples from A1-61 were analysed using TOF-SIMS. TOF-SIMS spectra measurements were carried out using a TOF-SIMS 5 instrument (ION-TOF GmbH, Germany). This instrument is equipped with a Bi liquid metal ion gun. Pulsed Bi⁺ primary ions have been predominantly used for analysis (25 keV, 0.3 pA). Analyses were performed semi-quantitatively using two settings: ‘mapping mode’ (500 μm × 500 μm) and in doing so removed using a second 17% HCl treatment, over 32 h and at 60 °C. The primary ion dose remained 4,000. The primary ion dose 

Cross-correlation. Chemical measurements of whole rocks and fossils were partitioned into 20-cm regular-spaced intervals between 2,125.1 and 2,459 m. Chemical measurements of each element were averaged within each interval and empty intervals (no measurements) were omitted from each time series. Averaged values were standardized to unit variance and a mean of zero before performing cross-correlation tests. Reported correlation coefficients are without temporal lag and non-parametric (Spearman’s Rho).

References

1. Munnecke, A., Calmer, M., Harper, D. A. T. & Servais, T. Ordovician and Silurian sea-water chemistry, sea level, and climate: a synopsis. Palaeogeogr. Palaeoclimatol. Palaeoecol. 296, 389–413 (2010).
2. Harper, D. A. T., Hammarlund, E. U. & Rasmussen, C. M. O. End Ordovician extinctions: a coincidence of causes. Geow. Rev. 25, 1294–1307 (2011).
3. Sheehan, P. M. The Late Ordovician mass extinction. Annu. Rev. Earth Planet. Sci. 29, 331–364 (2001).
4. Munnecke, A., Samtleben, C. & Bickert, T. The Ireviken Event in the lower Silurian of Gotland, Sweden—relation to similar Palaeozoic and Permo-Triassic events. Palaeogeogr. Palaeoclimatol. Palaeoecol. 195, 99–124 (2003).
5. Cramer, B. D. et al. P–zircon age constraints on the timing and duration of Wenlock (Silurian) paleocommunity collapse and recovery during the “Big Crisis”. Geol. Soc. Am. Bull. 124, 1841–1857 (2012).
6. Calner, M. In Mass Extinction (ed. A. M. T.) 21–57 (Springer Book, 2004).
7. Ghielen, J. F. et al. A Cenozoic-style scenario for the end-Ordovician glaciation. Nat. Commun. 5, 4485 (2014).
8. Cramer, B. D. & Saltzman, M. R. Early Silurian paired δ⁵³⁴⁴⁴⁴³⁴³⁴³⁴ Carbon and Nitrogen analyses from the Midcontinent of North America: implications for paleoceanography and paleoclimate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 256, 195–203 (2007).
9. Bickert, T., Pätzold, J., Samtleben, C. & Munnecke, A. Paleoenvironmental changes in the Silurian indicated by stable isotopes in brachiopod shells from Gotland, Sweden. Geochim. Cosmochim. Acta 61, 2277–2270 (1997).
10. McLaughlin, P. L., Embs, P. & Brett, C. E. Beyond black shales: the sedimentary and stable isotope records of oceanic anoxic events in a dominantly oxic basin (Silurian; Appalachian Basin, USA). Palaeogeogr. Palaeoclimatol. Palaeoecol. 367–368, 153–177 (2012).
11. Hammarlund, E. U. et al. A sulphidic driver for the end-Ordovician mass extinction. Earth Planet. Sci. Lett. 331–332, 128–139 (2012).
12. Embs, P. et al. The Ireviken Event: a Silurian OAE. Geol. Soc. Am. 42, 561 (2007).
13. Munnecke, A., Delabroye, A., Servais, T., Vandendriessche, T., R. A. & Vecoli, M. Systematic occurrences of malformed (teratological) acritarchs in the run-up of early Palaeozoic δ²⁶²¹²⁶²¹ Carbon isotope excursions. Palaeogeogr. Palaeoclimatol. Palaeoecol. 367–368, 137–146 (2012).
14. Delabroye, A., Munnecke, A., Servais, T., Vandendriessche, T., R. A. & Vecoli, M. Abnormal forms of acritarchs (phytoplankton) in the upper Hirnantian (Upper Ordovician) of Anticosti Island, Canada. Rev. Palaeobot. Palynol. 173, 46–56 (2012).
15. Owing to the exploratory nature of the study, the mapping-mode analyses used two different source modes, Bi⁺ and Bi²⁺. These are clearly separated in the Supplementary Dataset 1. For the ‘focused beam-mode’ analyses, only the Bi⁺ source was used (this is the data in Figs 3 and 4). The data from the ‘Bi²⁺ mapping mode’ clearly displays the same trend as for the ‘focused beam’ mode, that is, a clear increase in metals in the samples with teratological assemblages, compared with the other samples lower in the section (this is the bulk of the samples in Supplementary Dataset 1). For the ‘Bi²⁺ mapping mode’, this is somewhat less obvious (only three samples were analysed due to a markedly weaker signal), however, increases are observed for elements such as Fe, Al and Mo, in the chitinozoans of the two teratological samples analysed in Bi²⁺ mode.

Laser ablation-inductively coupled plasma-mass spectrometry. Major and trace element abundances for 32 bulk-sediment samples were determined by LA-ICP-MS at the USGS (Supplementary Dataset 3). Analyses are within 15% of accepted values of USGS reference materials, duplicate analyses of selected samples by ICP-AES and inductively coupled plasma-mass spectrometry and inductively coupled plasma-mass spectrometry (ICP-AES-MS) sodium peroxide sinter (SGS Mineral Services, Toronto) and in-house ICP-AES-MS sinter methods. Replicate analyses were <3% RSD.
15. Morin, S. et al. Long-term survey of heavy-metal pollution, biofilm contamination and diatom community structure in the Riou Mort watershed, South-West France. *Environ. Pollut.* 151, 532–542 (2008).
16. Falasco, E. et al. Morphological abnormalities of diatom silica walls in relation to heavy metal contamination and artificial growth conditions. *Water South Africa* 35, 595–606 (2009).
17. Elberling, B., Knudsen, K. L., Kristensen, P. H. & Asmussen, G. Applying foraminiferal stratigraphy as a biomarker for heavy metal contamination and mining impact in a fjord in West Greenland. *Mar. Environ. Res.* 55, 235–256 (2003).
18. Le Cadre, V. & Debenay, J. P. Morphological and cytological responses of *Daphnia magna* survival and performance in the water flea *Calanus chilensis* reproduction in a marine environment with high diatom concentration. *J. Exp. Mar. Biol. Ecol.* 352, 187–199 (2007).
19. Boenigk, J., Wiedbroth, A. & Pfandl, K. Heavy metal toxicity and bioavailability of dissolved nutrients to a bacterivorous flagellate are linked to suspended particle physical properties. *Aquat. Toxicol.* 71, 249–259 (2005).
20. Kobayashi, N. & Okamura, H. Effects of heavy metals on sea urchin embryo development. 1. Tracing the cause by the effects. *Chemosphere* 55, 1403–1412 (2004).
21. Di Riccio, A. et al. Deformities of chironomid larvae and heavy metal pollution: from laboratory to field studies. *Chemosphere* 112, 9–17 (2014).
22. Bengtsson, B. E. Biological variables, especially skeletal deformities in fish, for monitoring marine pollution. *Phil. Trans. R. Soc. Lond. B* 286, 457–464 (1979).
23. Sfakianakis, D. G., Renieri, E., Kentouri, M. & Tsatsakis, A. M. Effect of heavy metals on fish larvae deformities: a review. *Environ. Res.* 137, 246–255 (2015).
24. Navs, S., Waterkeyn, A., Voet, T., De Meester, L. & Brendonck, L. Pesticide exposure impacts not only hatching of dormant eggs, but also hatching survival and performance in the water flea *Daphnia magna*. *Ecotoxicology* 22, 803–814 (2013).
25. Poulet, S. A. et al. Collapse of *Calanus chilensis* reproduction in a marine environment with high diatom concentration. *J. Exp. Mar. Biol. Ecol.* 352, 187–199 (2007).
26. Chen, X., Mao, X., Cao, Y. & Yang, X. Use of siliceous algae as biological monitors of heavy metal pollution in three lakes in a mining city, southeast China. *Int. J. Oceanogr. Hydrobiol.* 42, 233–242 (2013).
27. Vandenbroucke, T. R. A. et al. Epipelagic chitinozoan biotopes map a steep latitudinal temperature gradient for earliest Late Ordovician seas: implications for a cooling Late Ordovician climate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 294, 202–219 (2010).
28. Servais, T., Stricarne, L., Montenari, M. & Press, J. Population dynamics of galeate acritarchs at the Cambrion-Ordovician transition in Algerian Sahara. *Palaeontologia* 47, 395–414 (2004).
29. Jaglin, J. C. & Paris, F. Exemples de téraitologie chez les chitinozoaires du Pridoli de Libye et implications sur la signification biologique du groupe. *Lethaia* 25, 151–164 (1992).
30. Le Hérisse, A. Palaeoecology, biostratigraphy and palaeogeography of late Silurian to early Devonian acritarchs and prasinophycean phycocysts in well A1-61, western Libya, North Africa. *Rev. Palaeobot. Palynol.* 118, 359–395 (2002).
31. Jaglin, J.-C. & Paris, F. Biostratigraphy, biodiversity and palaeogeography of late Silurian chitinozoans from A1-61 borehole (north-western Libya). *Rev. Palaeobot. Palynol.* 118, 335–358 (2002).
32. Mertens, K. N. et al. Process length variation in cysts of a dinoflagellate, *Lingulodinium machaerophorum*, in surface sediments: investigating its potential as salinity proxy. *Mar. Micropaleontol.* 70, 54–69 (2009).
33. Kaljo, D. et al. in *Global Events and Event Stratigraphy in the Phanerozoic* (ed Walliser, O. H.) 174–224 (Springer, 1995).
34. Cramer, B. D. et al. Revised correlation of Silurian Provincial Series of North America with global and regional chronostratigraphic units and δ13Ccarb chemostratigraphy. *Lethaia* 44, 185–202 (2011).
35. Jenkins, H. C. Geochemistry of oceanic anoxic events. *Geochim. Geophys. Geosyst.* 11, Q03004 (2010).
36. Calvert, S. E. & Pedersen, T. F. Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record. *Mar. Geol.* 113, 67–88 (1993).
37. Elderfield, H. & Greaves, M. The rare earth elements in seawater. *Nature* 296, 214–219 (1982).
38. Elderfield, H., Upstill-Goddard, R. & Sholkovitz, E. R. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochim. Cosmochim. Acta* 54, 971–991 (1990).
39. Mitra, A., Elderfield, H. & Greaves, M. Rare earth elements in submarine hydrothermal fluids and plumes from the Mid-Atlantic Ridge. *Mar. Chem.* 46, 217–235 (1994).
40. Sholkovitz, E. R., Shaw, T. J. & Schneider, D. L. The geochemistry of rare earth elements in the seasonally anoxic water column and porewaters of Chesapeake Bay. *Geochim. Cosmochim. Acta* 56, 3389–3402 (1992).
41. Johnson, C. A., Embslo, P., Poole, F. G. & Rye, R. O. Sulfur- and oxygen-isotopes in sediment-hosted strataform barite deposits. *Geochim. Cosmochim. Acta* 73, 133–147 (2009).
42. Embslo, P., McLaughlin, P. I., Breit, G. N., du Bray, E. A. & Koenig, A. E. Rare earth elements in sedimentary phosphate deposits: solution to the global REE crisis? *Gondwana Res.* 27, 776–785 (2015).
43. Diaz, R. J. & Rosenberg, R. Spreading dead zones and consequences for marine ecosystems. *Science* 321, 926–929 (2008).
44. Karlsson, A. W. et al. Historical trends in Chesapeake Bay dissolved oxygen based on benthic Foraminifera from sediment cores. *Estuaries* 23, 488–500 (2000).
45. Achab, A., Asselin, E., Desrochers, A., Riva, J. F. & Farley, C. Chitinozoan biostratigraphy of a new Upper Ordovician stratigraphic framework for Anticosti Island, Canada. *Geol. Soc. Am. Bull.* 123, 186–205 (2011).
46. Le Hérisse, A. Acritarches et kystes d’algues Prasinophyces du Silurien de Gotland. *Suède. Palaeontogr. Ital.* 76, 57–302 (1989).
47. Gempelr, P. *Practical Guide To Chemometrics* 2nd edn (CRC Press, 2006).

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**Author contributions**

T.R.A.V., P.E., A.M. and T.S. designed the project; T.R.A.V. performed palynological analyses; P.E. produced LA-ICP-MS data; N.N. and T.R.A.V. performed ToF-SIMS analyses; T.R.A.V., M.Q. and K.L. processed data; L.D. performed principal component analyses; W.K. performed cross-correlation analyses; F.P. provided samples; T.R.A.V., P.E., A.M. and W.K. wrote the paper.

**Additional information**

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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