Late Jurassic ocean anoxic event: evidence from voluminous sulphide deposition and preservation in the Panthalassa

Tatsuo Nozaki1,2,3, Yasuhiro Kato1,2,3,4 & Katsuhiko Suzuki2,3

1Department of Systems Innovation, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, 2Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan, 3Submarine Resources Research Project (SRRP), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan, 4Frontier Research Center for Energy and Resources (FRCER), School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

The historically productive copper-bearing Besshi-type sulphide deposits in the Japanese accretionary complex were formed as volcanogenic massive sulphide deposits on the deep-sea floor of the Panthalassa Ocean. Here we report that eleven typical Besshi-type deposits yielded Re-Os isochron ages around 150 Ma (148.4 ± 1.4 Ma from the composite isochron) in Late Jurassic time. This date coincides with the lowest marine 87Sr/86Sr ratio and highest atmospheric CO2 concentration of the past 300 million years. We infer that intense mid-ocean ridge hydrothermal and volcanic activity in the Late Jurassic produced huge sulphide deposits and large emissions of CO2 gas, leading to global warming and a stratified Panthalassa Ocean with anoxic deep seas that favored preservation of sulphides in the pelagic environment. The emergence of ocean anoxia triggered by seafloor volcanism is also consistent with a positive δ13C excursion and widespread deposition of petroleum source rocks and black shales.

Ocean anoxic events (OAEs) are recorded by the ubiquitous presence of organic carbon–rich sedimentary rocks such as black mudstone and shale, which are stable under anoxic conditions1–3. The presence of these rocks in pelagic deep-sea sedimentary successions in accretionary complexes is considered especially strong evidence for ancient OAEs on a global scale4–5, because pelagic deep-sea sediments far away from continents provide us representative information on open ocean environments. Similarly, sulphide minerals are redox-sensitive and easily dissolve in seawater under oxygenated conditions6–7. In the oxygenated pelagic deep-sea of open oceans such as the modern Pacific and Atlantic, seafloor hydrothermal sulphide deposits are rapidly dissolved or replaced by Fe-oxide or oxyhydroxide minerals6, and thus are not generally preserved. Hence, the presence of massive sulphide deposits, formed and preserved on an ancient pelagic deep-sea floor and now found in accretionary complexes, can be regarded as a powerful indicator of an OAE.

Our study involved the well-known copper-bearing sulphide deposits distributed along the Sanbagawa metamorphic belt of southwest Japan, a Cretaceous accretionary complex8,9. Classified as Besshi-type deposits, these large strata-bound (stratiform) sulphides were deposited within a limited stratigraphic range, perhaps only a few stratigraphic horizons, in a belt of outcrops more than 400 km long8 (Fig. 1). Besshi-type deposits are recognised throughout the world in rocks of Early Proterozoic to Paleogene age10–12. More than 100 Besshi-type deposits, including the type locality, have been documented in the Sanbagawa metamorphic belt (Fig. 1). These were a major source of copper during the development of modern Japan over approximately three centuries until the 1970s. Since the first discovery of a seafloor hydrothermal sulphide deposit on the East Pacific Rise13, many studies have established that Besshi-type deposits are ancient counterparts of modern volcanogenic massive sulphide (VMS) deposits related to mid-ocean ridge volcanism13–14. The deposits of the Sanbagawa metamorphic belt have yielded at least 60 Mt of documented ore plus substantial undocumented production, making them many times the size of the largest modern seafloor massive sulphide deposits, such as the Middle Valley (8.8 Mt15) and TAG (3.9 Mt16) hydrothermal deposits. The Pb and S isotope compositions of sulphide ores9 and the close association
of ore deposits with foot-wall basic schist (mid-ocean ridge basalt (MORB) in origin\(^1\)) and hanging-wall quartz schist (pelagic chert in origin\(^2\)) (Supplementary Fig. S1) indicate that the metal source of these Besshi-type VMS deposits (e.g., Cu and Zn) was hydrothermal fluids that circulated through MORB and deposited metal sulphides in ascending order; massive sulphide ore layers are within basic schist or between footwall basic schist and hanging-wall quartz schist\(^8,9,17\) (Supplementary Fig. S1). The basic stratigraphy of Besshi-type VMS deposits consists of basic schist (of MORB origin\(^1\)), quartz schist (of pelagic chert origin\(^2\)) and pelitic and psammitic schist in ascending order; massive stratigraphy of Besshi-type Sanbagawa high-P/T metamorphic belt. The Sanbagawa metamorphic belt is composed of pelitic and psammitic schist, basic schist, quartz schist, calcareous schist with some amounts of metagabbroic rock, peridotite and serpentinite (Supplementary Fig. S1). The basic stratigraphy of Besshi-type Sanbagawa high-P/T metamorphic belt. The Sanbagawa metamorphic belt contains almost no microfossils that could constrain the depositional age of its Besshi-type deposits. No other direct chronological constraints for such sulphide deposit have been published. One valuable tool for dating sulphide deposits is the \(^{187}\text{Re-}^{187}\text{Os}\) decay system, with a \(4.16 \times 10^{10}\) yr half-life period for \(\beta^-\) decay\(^18\), because both Re and Os are siderophile/chalcophile elements that tend to be concentrated into sulphide minerals, if they are undisturbed by metamorphism\(^20\rightarrow 22\). Thus, Re-Os ages can be used to directly determine the timing of sulphide mineralisation\(^20\rightarrow 22\). We applied the Re-Os dating method to obtain ages of 118 sulphide mineral samples from 11 Besshi-type deposits of the Sanbagawa metamorphic belt (Fig. 1).

**Results**

Re-Os isotope data from each Besshi-type deposit exhibit excellent linearity and wide variations in the \(^{187}\text{Re}/^{188}\text{Os}\) vs. \(^{187}\text{Os}/^{188}\text{Os}\) space (Fig. 2 and Supplementary Table S1). Over a range of more than 400 km from western Shikoku Island to the Kii Peninsula (Fig. 1), eleven Besshi-type deposits yielded a narrow range of Re-Os ages from 144.0 to 155.4 Ma, within the Late Jurassic epoch (Fig. 2). The Re-Os isochron plot for all 118 sulphide ore samples yielded an age of 148.4 ± 1.4 Ma (Fig. 2). No correlation was observed in the \(1/^{188}\text{Os/}^{187}\text{Os}\) space, strongly suggesting that these regression lines are not pseudo-isochrons produced by binary mixing of components with distinct Os-isotope profiles. The initial \(^{187}\text{Os}/^{188}\text{Os}\) ratios of the eleven deposits exhibited a wide range from \(0.1\) to \(0.67\) (Fig. 2).

These values are mostly greater than that of pristine hydrothermal fluid (\(0.12\)) and probably reflect entrainment of contemporaneous seawater with a higher \(^{187}\text{Os}/^{188}\text{Os}\) ratio (see details in Supplementary Information).

The Besshi-type deposits analysed here underwent high-P/T metamorphism up to 8–9.5 kbar and \(520 \pm 25\)°C\(^23,24\) (Supplementary Information). The sample analyses were not single-mineral separates but a composite of several sulphide minerals whose mode of occurrence is listed in Supplementary Table S1. Among these sulphide minerals, pyrite can yield reliable Re-Os ages from samples that underwent greenschist-facies metamorphism\(^25,26\) while retaining the primary Re-Os isotope composition from the time of its formation. Similarly, the Re-Os system in chalcopyrite is undisturbed by lower greenschist-facies metamorphism\(^26\). Most of our samples are dominated by pyrite or to a lesser extent chalcopyrite (Supplementary Table S1). However, some samples underwent lower epidote-amphibolite facies metamorphism and contain notable fractions of sphalerite and pyrrhotite, whose Re-Os isotope systems can
be easily disturbed by high-grade metamorphism\textsuperscript{27,28}. In order to examine the robustness of the Re-Os isotope system, five Re-Os isochron diagrams sorted by proportions of pyrite (less than 70\% and greater than 70\%, 80\%, 90\% and 95\%) are presented in Supplementary Fig. S2. We cannot rule out the possibility of minor disturbance of the Re-Os isotope system by high-P/T metamorphism on the ground that the mean square weighted deviation (MSWD) is largest with the pelagic nature of associated hanging-wall quartz schist, which has its origin in chert\textsuperscript{17}, confirming that the depositional sites of the sulphide deposits were in the open ocean of the Panthalassa. Thus, the sulphide samples studied here provide global geochronological signatures of paleocean environments just as do other pelagic sedimentary successions\textsuperscript{4}. Given that the Re-Os ages of the two largest deposits (Besshi and Sazare), which produced more than half of the massive sulphide took place mainly in a pelagic realm of the Panthalassa.

**Discussion**

The timing of Besshi-type sulphide deposition coincides with a major global marine Sr-isotope excursion in which the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio

![Figure 2](https://example.com/f2.png)

**Figure 2 |** Re-Os isochron diagrams for eleven Besshi-type sulphide deposits from the Sanbagawa metamorphic belt. Deposit numbers are shown in Fig. 1. A composite Re-Os isochron diagram for all Re-Os isotope data is also shown, constructed using the \(^{187}\text{Re}\) decay constant of 1.666 × 10\(^{-11}\) yr\(^{-1}\) (\(\pm 0.31\%\)) and Isoplot version 3\textsuperscript{9}. The composite Re-Os isochron age does not change if the most radiogenic sample (KK08) is omitted from the regression. Symbols in grey, yellow, blue and pink represent samples rich in pyrite, chalcopyrite, pyrrhotite and bornite, respectively. Mode of occurrence of each sulphide ore is given in Supplementary Table S1.
reached its lowest value of the past 300 Myr\textsuperscript{31,32} (Fig. 3). The low \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio indicates that the relative flux of hydrothermal fluid into seawater was at its greatest in the Late Jurassic. During this period of intense mid-ocean ridge activity, it is very likely that voluminous \(\text{CO}_2\) gas also entered the atmosphere as a result of seafloor volcanism. The atmospheric \(\text{CO}_2\) concentration in the Late Jurassic is estimated to be the highest of the past 300 Myr, nearly an order of magnitude higher than today\textsuperscript{33} (Fig. 3). Given this \(\text{CO}_2\) concentration, general circulation models (GCMs) indicate that the whole Earth including the deep oceans was as much as 10°C warmer than now and that polar ice sheets were absent or unstable for most of the Late Jurassic\textsuperscript{35}. Recent geochemical and isotope stratigraphy studies using \(\delta^{18}\text{O}, \delta^{13}\text{C}, ^{87}\text{Sr}/^{86}\text{Sr}\) and \(\text{Mg}/\text{Ca}\) ratios support an abrupt temperature rise during the Oxfordian age (157.3–163.5 Ma) of the Late Jurassic, followed by a prolonged warm period during the Kimmeridgian (152.1–157.3 Ma) and Tithonian (145.0–152.1 Ma) ages\textsuperscript{35,36}. The warm conditions inevitably reduced the temperature gradient between equatorial and polar regions\textsuperscript{37}, leading to the decrease or disappearance of polar ice sheets\textsuperscript{38}. The inhibition of ice formation in turn would have subdued global ocean circulation and led to the development of stagnant anoxic deep seas. We suggest that intense hydrothermal activity at a mid-ocean ridge during the Late Jurassic induced anoxic conditions in the pelagic Panthalassa Ocean and contributed to the formation of Besshi-type sulphide deposits as well as their preservation from dissolution in seawater.

The existence of a Late Jurassic OAE was proposed for the Tethys Ocean by some previous studies\textsuperscript{38,39}, but such an OAE has not yet been documented for the contemporaneous Panthalassa Ocean. The global prevalence of the Late Jurassic OAE is consistent with widespread deposition of Late Jurassic black shales in the North Sea, Gulf of Mexico, eastern Greenland, western South America (Peru) and the Siberian Basin\textsuperscript{40}. Moreover, the Late Jurassic was probably the greatest period of organic-carbon burial and petroleum source-rock sedimentation of the entire Phanerozoic eon\textsuperscript{41,42}. Enhanced carbon burial is supported by a positive \(\delta^{13}\text{C}\) excursion in carbonate successions from this period\textsuperscript{43,44}. The geologic and geochemical lines of evidence mentioned here consistently indicate that large scale ocean anoxia occurred during the Late Jurassic\textsuperscript{46}. The development of anoxic deep ocean would have played a key role in preserving Besshi-type massive sulphide deposits, as well as petroleum source rocks and black shales, on the deep-sea floor of the Panthalassa Ocean.

We conclude that Besshi-type deposits in the Sanbagawa metamorphic belt were produced primarily by intense seafloor hydrothermal activity at a mid-ocean ridge, then preserved under stagnant anoxic conditions as they were gradually covered by pelagic chert (now metamorphosed as quartz schist), and then accreted onto the paleo-Japanese Islands. Therefore, the Sanbagawa Besshi-type VMS can be regarded as the consequence of a newly documented Late Jurassic OAE affecting the Panthalassa Ocean as well as the Tethys Ocean\textsuperscript{8,39}. The Late Jurassic period is characterised by unique OAE phenomena such as deposition and preservation of massive sulphides, pervasive deposition of petroleum source rocks and black shales, and an extreme low in marine Sr isotope ratio; however, the mass extinction in the Late Jurassic (mainly Kimmeridgian) is not as severe as the end-Permian or Triassic–Jurassic mass extinctions\textsuperscript{44,45}. Further chemostratigraphic studies targeting pelagic sedimentary successions in the circum-Panthalassa area should reveal details of the Late Jurassic OAE such as its duration, magnitude and prevalence.

Age determination of VMS deposits formed on the pelagic deep sea floor using the Re-Os dating method opens up a new approach for unravelling the relationship and interplay between global OAEs and massive sulphide deposition and preservation. In addition, the depositional age constraint obtained here may help guide mineral exploration and lead to the discovery of Besshi-type deposits in accretionary complexes elsewhere in the world.

*Figure 3* | Timing of Besshi-type VMS deposition with marine Sr-isotope, Os-isotope and atmospheric CO\(_2\) curves. Secular change of marine \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio\textsuperscript{31,32}, \(^{187}\text{Os}/^{188}\text{Os}\) ratio\textsuperscript{60} and mass ratio of atmospheric \(\text{CO}_2\) compared to present\textsuperscript{33} (RCO\(_2\)) are shown from the Permian to the present together with major ocean anoxic events (OAEs). The Late Jurassic OAE in the Panthalassa Ocean is proposed in this paper.
Methods
Sample collection and preparation. Sulphide ore samples were collected from eleven Besshi-type sulphide deposits (from west to east: Takaura, Kaki, Nii, Besshi, Iyo, Shiratake, Marukobetsu, Kotsu and Higashiyama deposits on Shikoku Island and limoni on the Kii Peninsula of Honshu Island) in the Sanbagawa metasomagic belt, Japan (Fig. 1). Sulphide samples of four Besshi-type deposits (Besshi, Sazare, Kotsu and limoni) were provided by the University Museum of the University of Tokyo, and the other samples of seven deposits were obtained during our field investigation. The deposits are massive/banded ores, except for the Takaura deposit, which includes some disseminated ores. They are mostly fine-grained and dominated by pyrrhotite, whereas some of the museum samples are high-grade copper ores mainly composed of chalcopyrite, bornite and minor chalcocite (Supplementary Table S1). Under the reflecting microscope, constituent sulphide minerals are pyrite, chalcopyrite and sphalerite with minor pyrrhotite, bornite, covellite, chalcocite, cobaltite and galena.

Fresh sulphide fragments were hand-picked to avoid contamination by weathered materials or veins and then rinsed with Milli-Q deionised water in an ultrasonic bath for at least 30 min. They were then crushed in an agate mortar and passed through a 630 μm sieve (< 350 μm). The samples were separated using di-iodomethane heavy liquid (CH2I2–Yamagishima Pharmaceutical Co. Ltd., Japan) to remove gangue silicate minerals, then washed three times in an ultrasonic acetone bath. Other silicate minerals (mostly quartz) were typically less than 2% by volume, and their Re and Os concentrations were below the detection limit, making their contribution to the Re-Os system negligible.

Re-Os isotope analyses. Our Re-Os analytical procedures are fully described elsewhere44,45. All measurements were performed using a negative thermal ionisation mass spectrometer (N-TIMS: ThermoFinnigan TRITON) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). Re and Os concentrations were determined by an isotope dilution method combined with Carus tube digestion54. CCl4 and HBr extraction of Os55,56. Os purification by microdistillation57, and Re separation by anion exchange chromatography58. Approximately 50–500 mg of separated sulphide sample was weighed, spiked with 190Re and 186Os, and digested in 10 ml inverse aqua regia in a sealed Carus tube at 220 °C for 24 h. After cooling, the solution was transferred to 30-mL PFA vessels into which 4 mL CCl4 was added to extract Os. This mixture was shaken for 2 min, and the CCl4 was transferred to 20-mL PFA vessels after centrifugation. This CCl4 extraction was performed three times and was followed by the addition of 4 mL HBr to the Os-bearing CCl4 solution, which was warmed under a heat lamp for 1 h. The Os-bearing HBr fraction was gently evaporated and purified by microdistillation. Re was separated from the aqueous phase remaining after the CCl4 extraction of Os in a Muromac AG 1-X8 anion exchange resin.

Re and Os isotopic compositions were measured in static multiple Faraday collector mode and pulse-counting electron multiplier mode, respectively. From the measured oxide ratios of ReO4– and OsO42–, atomic ratios of Re and Os were calculated after correction for oxide interference. Oxide corrections were made using (190Re/187Os = 0.00037 and 188Os/186Os = 0.002045). Instrumental mass fractionation of Os was corrected against a stable 190/188Os ratio of 3.082715. For precise analysis of Re isotope measurements, all analyses were performed using a negative thermal ionisation mass spectrometer (N-TIMS: ThermoFinnigan TRITON) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The internal structure of an active sea-floor massive sulphide deposit in the Sanbagawa metamorphic belt, Japan. Geochim. Cosmochim. Acta 74, 4322–4331 (2010).

Smollar, M. I., Walker, R. J. & Morgan, J. W. Re-Os ages of group IIA, IIIA, IVA, and IVB iron meteorites. Science 271, 519–513 (1996).

Stein, H. J., Markey, R. J., Morgan, J. W., Hannah, J. L. & Schersteën, A. The remarkable Re-Os chronometer in molybdenite: how and why it works. Terra Nova 13, 479–486 (2001).

Banno, S. & Sakai, C. Geology and metamorphic evolution of the Sanbagawa metamorphic belt, Japan. Geol. Soc. Spec. Pap. 43, 519–532 (1989).

Eman, R., Wallas, S. R. & Banno, Y. Paragenesis of sodic pyroxene-bearing quartzitic cherts: implications for the P-T history of the Sanbagawa belt. Contrib. Mineral. Petrol. 116, 182–198 (1994).

Brenan, J. M., Chenriak, D. J. & Rose, L. A. Diffusion of osmium in pyrrhotite and pyrite: implications for closure of the Re-Os isotopic system. Earth Planet. Sci. Lett. 180, 399–413 (2000).

Selby, D., Kelley, K. D., Hitzman, M. W. & Zieg, J. Re-Os sulphide (bornite, chalcopyrite, and pyrite) systematics of the carbonate-hosted copper deposits at Ruby Creek, southern Brooks Range, Alaska. Econ. Geol. 104, 437–444 (2009).

Morelli, R. M. et al. Re-Os sulfide geochronology of the Red Dog sediment-hosted Zn-Pb-Ag deposit, Brooks Range, Alaska. Econ. Geol. 99, 1569–1576 (2004).

Morelli, R. M., Bell, C. C., Creaser, R. A. & Simonetti, A. Constraints on the genesis of gold mineralization at the Homestake Gold Deposit, Black Hills, South Dakota from rhenium-osmium sulfide geochronology. Mineral. Deposita 45, 461–480 (2010).

Okamoto, K. et al. SHRIMP U-Pb zircon dating of quartz-bearing eclogite from the Sanbagawa Belt, south-west Japan: implications for metamorphic evolution of subducted protolith. Terra Nova 16, 81–89 (2004).

Wallas, S. R. et al. Plate movements, ductile deformation and geochronology of the Sanbagawa belt, SW Japan: tectonic significance of 89–88 Ma Lu-Hf eclogite ages. Terra Nova 13, 112–149 (2001).

McArthur, J. M., Howarth, R. J. & Bailey, T. R. Stromatolite isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma and accompanying look-up table for deriving numerical age. J. Geol. 109, 155–170 (2001).

Berner, R. A. & Kothavala, Z. GEOCARB III: A revised model of atmospheric CO2 over Phanerozoic time. Am. J. Sci. 301, 182–204 (2001).

Eilbom, H. W. & Valdes, P. J. Jurassic climates. Proc. Geol. Assoc. 119, 5–17 (2008).

Price, G. D. & Rogov, M. A. An isotopic appraisal of the Late Jurassic greenhouse phase in the Russian Platform. Palaeogeogr. Palaeoclimatol. Palaeoecol. 273, 41–49 (2009).
36. Nunn, E. V. & Price, G. D. Late Jurassic (Kimmeridgian-Tithonian) stable isotopes (δ18O, δ13C) and Mg/Ca ratios: New palaeoclimatic data from Hemsdale, northeast Scotland. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **292**, 325–335 (2010).

37. Große, D. R., Price, G. D., Ruffell, A. H., Mutterlose, J. & Baraboshkin, E. Isotopic evidence for Late Jurassic-Early Cretaceous climate change. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **202**, 97–118 (2003).

38. Podlaha, O. G., Mutterlose, J. & Veizer, J. Preservation of δ18O and δ13C in belemnite rostra from the Jurassic Early Cretaceous successions. *Am. J. Sci.* **298**, 324–347 (1998).

39. Pearce, C. R., Coe, A. L. & Cohen, A. S. Seawater redox variations during the deposition of the Kimmeridge Clay Formation, United Kingdom (Upper Jurassic): Evidence from molybdenum isotopes and trace metal ratios. *Palaeoceanography* **25**, PA4123, doi:10.1029/2010PA001963 (2010).

40. Moore, G. T., Hayashida, D. N., Ross, C. A. & Jacobson, S. R. Paleoclimate of the Jurassic: Evidence from molybdenum isotopes and trace metal ratios. *Palaeoceanography* **25**, PA4123, doi:10.1029/2010PA001963 (2010).

41. Klemme, H. D. & Ulmishek, G. F. Effective petroleum source rocks of the world - stratigraphic distribution and controlling depositional factors. *AAPG Bull.* **75**, 1809–1851 (1991).

42. Vyshemirskii, V. S. & Kontorovich, A. E. Cyclic character of oil accumulation in the earth's history. *Geologiya Geofizika* **38**, 907–918 (1997).

43. Weissert, H. & Mohr, H. Late Jurassic climate and its impact on carbon cycling. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **122**, 27–43 (1996).

44. Raup, D. M. & Sepkoski, J. J. Mass extinctions in the marine fossil record. *Proc. Natl. Acad. Sci. USA* **81**, 801–805 (1984).

45. Raup, D. M. & Sepkoski, J. J. Periodicity of extinctions in the geologic past. *Science* **215**, 1501–1503 (1982).

46. Raup, D. M. & Sepkoski, J. J. The periodicity of extinctions in the geologic past. *Proc. Natl. Acad. Sci. USA* **81**, 801–805 (1984).

47. Suzuki, K. & Tatsumi, Y. Re-Os systematics of high-Mg andesites and basalts from the Andaman Islands. *Geochim. Cosmochim. Acta* **67**, 3673–3686 (2003).

48. Isozaki, Y., Aoki, K., Nakama, T. & Yanai, S. New insight into a subduction-related orogen: A reappraisal of the geotectonic framework and evolution of the Japanese Islands. *Gondwana Res.* **18**, 82–105 (2010).

49. Shirey, S. B. & Walker, R. J. Carius tube digestion for low-blank rhenium-osmium isotope analysis. *Anal. Chem.* **63**, 297–307 (2001).

50. Cohen, A. S. & Waters, G. G. Separation of osmium from geological materials by solvent extraction for analysis by thermal ionization mass spectrometry. *Anal. Chem.* **63**, 278–288 (1991).

51. Birck, J. L., Roy-Barman, M. & Capmas, F. Re-Os isotopic measurements at the femt mole level in natural samples. *Geost. Newslett.* **21**, 19–27 (1997).

52. Roy-Barman, M. & Allegre, C. J. 187Os/188Os ratios of midocean ridge basalts and abyssal peridotites. *Geochim. Cosmochim. Acta* **58**, 5043–5054 (1994).

53. Morgan, J. W., Golightly, D. W. & Dorrapot, A. F. Methods for the separation of rhenium, osmium and molybdenum applicable to isotope geochemistry. *Talanta* **38**, 259–265 (1991).

54. Nier, A. O. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Phys. Rev.* **77**, 789–793 (1950).

55. Nier, A. O. The isotopic constitution of osmium. *Phys. Rev.* **52**, 885–885 (1937).

56. Suzuki, K., Miyata, Y. & Kanazawa, N. Precise Re isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS) using total evaporation technique. *Int. J. Mass Spectrom.* **235**, 97–101 (2004).

57. Stein, H., Scherstén, A., Hannah, J. & Markey, R. Sub-grain scale decoupling of Re and 187Os and assessment of laser ablation ICP-MS spot dating in molybdenite. *Geochim. Cosmochim. Acta* **67**, 3673–3686 (2003).

58. Isozaki, Y., Aoki, K., Nakama, T. & Yanai, S. New insight into a subduction-related orogen: A reappraisal of the geotectonic framework and evolution of the Japanese Islands. *Gondwana Res.* **18**, 82–105 (2010).

59. Ludwig, K. R. Isoplot/Ex, version 3: A geochronological toolkit for Microsoft Excel: Berkeley, California, Geochronology Center Berkeley (2003).

60. Peucker-Ehrenbrink, B. & Ravizza, G. In The geologic time scale 2012 (eds Gradstein, F. M., Ogg, J. G., Schmitz, M. & Ogg, G.) 145–166 (Elsevier, Amsterdam, 2012).

**Acknowledgements**

Some sulphide ore samples were kindly provided by the University Museum, the University of Tokyo. This research was supported by the Japan Society for the Promotion of Science through Grants-in-Aid Nos. 15204048 and 17403012 to Y.K., Nos. 07802470 and 21840069 to T.N. and Nos. 20109006 and 20340158 to K.S. We thank Y. Takaya, H. Osawa, K. Fujinaga, T. Nishichui, H. Abe, R. Senda, H. Yamamoto, Y. Otsuki, S. Senshu and T. Sato for their assistance with field investigations, sample preparations and chemical analyses. The manuscript was much improved by constructive comments from J.-I. Kimura, A. Ishikawa, J. Kuroda, Y. Sekine and H. Iwamoto.

**Author contributions**

Y.K. developed the conceptual idea for this study, T.N. did field work and sample preparations, and T.N. and K.S. conducted the Re-Os isotope analyses. All authors contributed to discussions and the writing of the manuscript.

**Additional information**

*Supplementary information* accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

*License:* This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0/

**How to cite this article:** Nozaki, T., Kato, Y. & Suzuki, K. Late Jurassic ocean anoxic event: evidence from voluminous sulphide deposition and preservation in the Panthalassa. *Sci. Rep.* **3**, 1889; DOI:10.1038/srep01889 (2013).