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

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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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and highest atmospheric CO_2 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 CO_2 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 $\delta^{13}\text{C}$ 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 conditions^{1–3}. 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 scale^{2–4}, 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 conditions^{5–7}. 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 minerals^{6,7}, 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 complex^{8,9}. 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 long¹⁰ (Fig. 1). Besshi-type deposits are recognised throughout the world in rocks of Early Proterozoic to Paleogene age^{11,12}. 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 volcanism^{8,9,14}. 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

Figure 1 | Sample location map with geotectonic subdivisions of southwest Japan. All Besshi-type deposits sampled for this study (stars) are in the 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 VMS deposits consists of basic schist (of MORB origin¹⁴), quartz schist (of pelagic chert origin¹⁷) and pelitic and psammitic schist 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). Abbreviations: b. = belt, mb. = metamorphic belt, ATL = Aki Tectonic Line, BTL = Butsuzo Tectonic Line, I-KTL = Ishigaki-Kuga Tectonic Line, MTL = Median Tectonic Line. Modified from ref. 58.

of ore deposits with foot-wall basic schist (mid-ocean ridge basalt (MORB) in origin¹⁴) and hanging-wall quartz schist (pelagic chert in origin¹⁷) (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 on a pelagic seafloor in the Panthalassa Ocean^{17,18}.

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 deposition have been published. One valuable tool for dating sulphide deposits is the ¹⁸⁷Re–¹⁸⁷Os decay system, with a 4.16×10^{10} yr half-life period for β^- decay¹⁹, because both Re and Os are siderophile/chalcophile elements that tend to be concentrated into sulphide minerals, if they are undisturbed by metamorphism^{20,21}. Thus, Re–Os ages can be used to directly determine the timing of sulphide mineralisation^{20–22}. 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 ¹⁸⁷Re/¹⁸⁸Os vs. ¹⁸⁷Os/¹⁸⁸Os 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 ¹⁸⁷Os/¹⁸⁸Os vs. ¹⁸⁷Os/¹⁸⁸Os space, strongly suggesting that these regression lines are not pseudo-isochrons produced by binary mixing of components with distinct Os-isotope profiles. The initial ¹⁸⁷Os/¹⁸⁸Os 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 ¹⁸⁷Os/¹⁸⁸Os ratio (see details in Supplementary Information).

The Besshi-type deposits analysed here underwent high-P/T metamorphism up to 8–9.5 kbar and $520 \pm 25^\circ\text{C}$ ^{23,24} (Supplementary Information). The sample analytes 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 metamorphism²⁶. 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

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}Re decay constant of $1.666 \times 10^{-11} \text{ yr}^{-1} (\pm 0.31\%)^{19}$ and Isoplot version 3⁵⁹. 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.

be easily disturbed by high-grade metamorphism^{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 for the less-than-70% pyrite isochron and the MSWD of the more-than-95% pyrite isochron still greatly exceeds 1. Regardless of their pyrite fractions, however, the five Re-Os isochron plots yielded the same ages within their uncertainties. Several high MSWD values in the isochron plots (Fig. 2 and Supplementary Fig. S2) may partly reflect variability in the initial $^{187}\text{Os}/^{188}\text{Os}$ ratios retained in sulphide minerals, which can be expected to range between those of Late Jurassic seawater and pristine hydrothermal fluids (see details in Supplementary Information). In sum, these sulphide samples preserve an original pre-metamorphism Re-Os isotope signature, and the Re-Os ages of the sulphide ores can be determined precisely owing to the wide range in their $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios (Fig. 2 and Supplementary Table S1), thus their isochron ages can be considered equivalent to the timing of sulphide deposition on a paleo-seafloor. Indeed, all Re-Os ages of the eleven Besshi-type deposits are much older than the age of peak metamorphism in the Sanbagawa metamorphic belt (110–120 Ma²⁹ or 90 Ma³⁰), which corresponds to their emplacement in the subduction zone. This

distinct age gap between formation and metamorphism, and the concordant Re-Os ages among the eleven Besshi-type deposits, both also attest to the robustness of the Re-Os isotope system during high-P/T metamorphism.

From the geologic history of the Sanbagawa metamorphic belt^{17,18} and the Re-Os ages reported here, we estimate that the sulphide deposits took between 70 and 25 Myr to travel from their primary depositional sites to the subduction zone. This estimation is consistent with the pelagic nature of associated hanging-wall quartz schist, which has its origin in chert¹⁷, 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 geochemical signatures of paleocean environments just as do other pelagic sedimentary successions^{2–4}. Given that the Re-Os ages of the two largest deposits (Besshi and Sazare), which produced more than half of the ore from the Sanbagawa metamorphic belt, are 153.2 ± 3.0 and 153.4 ± 3.6 Ma, respectively (Fig. 2), we conclude that deposition of massive sulphide took place mainly in a pelagic realm of the Panthalassa Ocean during the Kimmeridgian age (152.1–157.3 Ma) in the Late Jurassic epoch.

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

reached its lowest value of the past 300 Myr^{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 CO_2 gas also entered the atmosphere as a result of seafloor volcanism. The atmospheric 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 today³³ (Fig. 3). Given this 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 Jurassic³⁴. Recent geochemical and isotope stratigraphy studies using $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and Mg/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^{35,36}. The warm conditions inevitably reduced the temperature gradient between equatorial and polar regions³⁷, leading to the decrease or disappearance of polar ice sheets³⁴. 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^{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 Basin⁴⁰. Moreover, the Late Jurassic was probably the greatest period of organic-carbon burial and petroleum source-rock

sedimentation of the entire Phanerozoic eon^{41,42}. Enhanced carbon burial is supported by a positive $\delta^{13}\text{C}$ excursion in carbonate successions from this period^{35,38,43}. The geologic and geochemical lines of evidence mentioned here consistently indicate that large scale ocean anoxia occurred during the Late Jurassic³⁹. 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^{38,39}. 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^{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^{31,32}, $^{187}\text{Os}/^{188}\text{Os}$ ratio⁶⁰ and mass ratio of atmospheric CO_2 compared to present³³ (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, Kuki, Nii, Besshi, Iyo, Shirataki, Shimokawa, Sazare, Kotsu and Higashiyama deposits on Shikoku Island and Iimori on the Kii Peninsula of Honshu Island) in the Sanbagawa metamorphic belt, Japan (Fig. 1). Sulphide samples of four Besshi-type deposits (Besshi, Sazare, Kotsu and Iimori) 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 pyrite, 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 #60 sieve (< 350 µm). The samples were separated using di-iodomethane heavy liquid (CH₂I₂; Yanagishima 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 elsewhere^{18,46–48}. 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 Carius tube digestion⁴⁹, CCl₄ and HBr extraction of Os^{50,51}, Os purification by microdistillation⁵², and Re separation by anion exchange chromatography⁵³.

Approximately 50–500 mg of separated sulphide sample was weighed, spiked with ¹⁸⁵Re and ¹⁹⁰Os, and digested in 10 mL inverse aqua regia in a sealed Carius 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 isotope compositions were measured in static multiple Faraday collector mode and pulse-counting electron multiplier mode, respectively. From the measured oxide ratios of ReO₄[−] and OsO₃[−], atomic ratios of Re and Os were calculated after correction for oxide interference. Oxide corrections were made using ¹⁷O/¹⁶O = 0.00037 and ¹⁸O/¹⁶O = 0.002045⁵⁴. Instrumental mass fractionation of Os was corrected against a stable ¹⁹²Os/¹⁸⁸Os ratio of 3.08271⁵⁵. For precise analysis of Re isotope composition, a total evaporation method⁵⁶ was applied to eliminate the effect of instrumental mass fractionation during the measurement. The total procedural blank was ~ 7 pg for Re and ~ 2 pg for Os with a ¹⁸⁷Os/¹⁸⁸Os ratio of ~ 0.15. The precision of the ¹⁸⁷Os/¹⁸⁸Os measurements, based on analysis of a Johnson Matthey Company Os standard solution (JMC; Alfa Aesar 1,000 ppm ICP Os standard solution) over a period of several months, was better than 0.4% (2σ).

Fine-grained sulphide samples (< 350 µm) were separated by using CH₂I₂ heavy liquid. Since fine-grained sulphide minerals such as chalcopyrite may adsorb/absorb Re and Os from the heavy liquid⁵⁷, we first checked the Re and Os concentrations of the heavy liquid. The Re and Os concentrations were 4.54 ± 1.04 and 1.19 ± 0.46 ppt (n = 5; avg. ± 1σ)¹⁸, respectively, much lower than those of the sulphide samples (Supplementary Table S1). Moreover, the sulphide separates were carefully washed three times in an ultrasonic acetone bath; thus, the heavy liquid separation using CH₂I₂ did not affect our Re-Os results. In fact, ref. 48, a study that used the same heavy liquid for mineral separation, reported no systematic differences in the Re and Os contents of separated sulphide samples with or without the heavy liquid separation, and found that all such sulphide separates yielded a well-defined isochron. All Re-Os data of the 118 sulphide ore samples from eleven Besshi-type deposits are given in Supplementary Table S1 online.

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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

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