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Final assembly of Gondwana enhances crustal metal (HREE and U) endowment

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Supplementary Information

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- Analytical Methods
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Sample Descriptions

Three samples containing uraninite (sample 1804YS04), xenotime (sample1605YS04), and hingganite-[Y] (sample 1804YS10) for U-Pb dating, and Sm-Nd isotope analysis were collected from the lower part of the bedded orebody. Fourteen samples (Ys01-14) of sulfide bulk ore were collected from the lower to the upper part of the bedded orebody. Five samples (20YS11, 23, 26, 29, and 32) with clastic xenotime and one sample (20YS28) with detrital zircon of red sandstone for U-Pb dating, and sixteen samples of red sandstone for bulk-rock Sm-Nd isotope analysis were collected from the footwall red sandstone (sampling locations are shown in Fig. S-5). The xenotime, hingganite-[Y], and uraninite samples were prepared as polished sections for element mapping, U-Pb dating, Sm-Nd analysis. Detrital zircon samples were handpicked under a binocular microscope, mounted in an epoxy resin disc, and then polished for U-Pb dating analysis. Hingganite-[Y] and xenotime in the bedded mineralisation occur as subhedral to anhedral grains, uraninite occurs as elongated aggregates (Figs. 1c–g and S-4d, e), and detrital zircon in the sandstone occur as euhedral to subhedral grains. The xenotime, hingganite-[Y], and uraninite samples were prepared as polished sections for element mapping and U-Pb dating analysis. The element mapping of xenotime was carried out by electron probe microanalysis (EPMA), and the U-Pb data were acquired by LA-ICP-MS. *In-situ* xenotime and hingganite-[Y], and bulk-rock Sm-Nd isotope data were acquired by LA-MC-ICP-MS and MC-ICP-MS, respectively.



Analytical Methods

μ -XRF element mapping

Element mapping was carried out at Guangzhou Tuoyan Analytical Technology Co., Ltd., China, using a Bruker's M4 Tornado Plus μ -XRF spectrometer. The X-ray generator was operated at 50 kV and 300 μ A and a composition of filters was used to reduce the background. All measurements were carried out under 2 mbar vacuum conditions and directly on the samples which were placed on the μ -XRF platform with pixel distance for 18 μ m and a 5 ms time per pixel. Evaluation of the data and preparation of element distribution maps were done using M4 TORNADO software provided by Bruker Nano Analytics.

SEM and mineral and element mapping

Mineral/phase distribution maps were obtained on thin sections using a TESCAN Integrated Mineral Analyser (TIMA3 GHM) system at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, China. The measurements were performed with the dot-mapping mode. Pixel spacing (BSE) was set to 3 μ m and dot spacing (EDS) was set to 9 μ m. All measurements were done at 25 kV with a spot size of 50 nm in high-vacuum mode, a working distance of 15 mm and beam current of 5 nA. EPMA element mapping was carried out using a JEOL JXA-8230 electron microprobe with an accelerating voltage of 15 kV, beam current of 50 nA, and beam diameter of 1 μ m.

LA-ICP-MS U-Pb xenotime dating

U-Pb isotopic analysis of xenotime hosted in the bedded/massive mineralisation was carried out using an Analytikjena M90 quadrupole ICP-MS equipped with a 193 nm NWR193 Ar-F excimer laser at Yanduzhongshi Geological Analysis Laboratories, China. Each analysis incorporated a background acquisition of approximately 20 s followed by 40 s of data acquisition from the sample. Each analysis was performed with a spot size diameter of 15 µm at 7 Hz with an energy of 4 J/cm². The reference xenotime material (MG-1) was analysed twice for every six analyses as an external standard, and the xenotime reference (BS-1, 513.6 ± 4.5 Ma; Liu *et al.*, 2011) was analysed once for every six analyses as a control standard sample to check age reproducibility. U-Pb isotope analysis of xenotime hosted in the red sandstone was done using an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled with a 193 nm Ar-F excimer laser system (Geolas HD, Göttingen, Germany) at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Each analysis was performed with a spot size of 10 µm at 2 Hz with an energy of 5 J/cm². Possible surface contamination was avoided by pre-ablation with two laser pulses. More details are given in Wu et al. (2020). The reference xenotime material (MG-1) was analysed twice for every six analyses as an external standard, and the xenotime reference (BS-1) was analysed once for every six analyses as a control standard to check age reproducibility. All measured isotope ratios of the MG-1 reference material during analyses were regressed and corrected via the method of Liu et



al. (2011). Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software (Griffin *et al.*, 2008). The U-Pb ages and weighted mean ages were calculated using the ISOPLOT 3.0 software package (Ludwig, 2003).

LA-ICP-MS uraninite U-Pb dating

U-Pb dating of uraninite was conducted by LA-ICP-MS at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China, using an Agilent 7700e ICP-MS instrument coupled with a GeolasPro laser ablation system. Each analysis was performed with a spot size diameter of 10 µm at 1 Hz. Uraninite reference material (GBW04420) was used as an external standard for U-Pb isotope calibration. Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition for the sample. The U-Pb ages were processed by ICPMSDataCal software (Liu *et al.*, 2008), and the calculation of U-Pb ages was performed by the ISOPLOT 3.0 software package (Ludwig, 2003).

LA-MC-ICP-MS Sm-Nd isotope analysis

Neodymium isotopic ratios of hingganite-[Y] and xenotime were analysed by LA-MC-ICP-MS at Nanjing FocuMS Technology Co. Ltd, Jiangsu province, China, using a Nu Instruments *Nu Plasma II* MC-ICP-MS coupled with a RESOlution 193-nm ArF Excimer Laser Ablation system. For hingganite-[Y] and xenotime Sm-Nd isotope analyses, each acquisition incorporated 20 s background (gas blank). Each analysis was performed with a spot size diameter of 75 μ m at 5 Hz with an energy of 4.5 J/cm². To correct for this interference of ¹⁴⁴Sm on ¹⁴⁴Nd, the ¹⁴⁷Sm/¹⁴⁹Sm ratio (1.0868) and the measured ¹⁴⁷Sm/¹⁴⁹Sm ratios are for calculating the Sm fractionation factor, and then the measured ¹⁴⁷Sm intensity and the natural ¹⁴⁷Sm/¹⁴⁴Sm ratios are used for correcting the Sm interference on mass 144. The interference-corrected ¹⁴⁶Nd/¹⁴⁴Nd ratios were then normalised to 0.7219 for calculating the Nd fractionation factor. The ¹⁴³Nd/¹⁴⁴Nd and ¹⁴⁵Nd/¹⁴⁴Nd ratios were normalised via the exponential law. Standard monazites (Trebilcock, M4, 44069, M2 and Namaqualand-2) and apatites (AP1, MAD, OtterLake, Durango, and AP2) were used as quality control for every ten unknown samples. Similarly, the ¹⁴⁷Sm/¹⁴⁴Nd ratios were calculated by the exponential law after correction of the isobaric interference of ¹⁴⁴Sm on ¹⁴⁴Nd, and ¹⁴³Sm/¹⁴⁴Nd ratios were calculated monazite (Namaqualand-2, ¹⁴⁷Sm/¹⁴⁴Nd = 0.0980 ± 3; Liu *et al.*, 2012).

Bulk-rock Nd isotope analysis

High-precision Nd isotope measurements were done at Nanjing FocuMS Technology Co. Ltd, Jiangsu province (China), using a Nu Instruments Nu Plasma II MC-ICP-MS. Rock powders were mixed with 0.5 mL 60 wt. % HNO₃ and 1.0 mL 40 wt. % HF in high-pressure PTFE bombs. Digested samples were dried down on a hotplate and reconstituted in 1.5 mL of 1.5 N HCl before ion exchange purification. Biorad AG50W-X8 cation exchange column was for roughly separating Sr and REE. High-field-strength-elements were washed out by 1.5 N HCl, and matrix elements (Na, Mg, K, Ca) and Rb were followed by 2.0 N HCl; then the Sr and



REE fractions were washed out by 2.5 and 6.0 N HCl, respectively. After that REE fractions were dried down, re-dissolved in 0.12 N HCl, and loaded onto LN-specific columns. La, Ce, and Pr were washed out by 0.12 N HCl, and then Nd and Sm were eluted by 0.18 and 0.4 N HCl, respectively. Small aliquots of each sample solution were analysed for exacting element concentration by Agilent Technologies 7700x quadrupole ICP-MS. Raw data of Nd isotope ratios were corrected for mass fractionation via normalising to 146 Nd/ 144 Nd = 0.7219 with exponential law. An isotope standard (JNdi-1) was used to correct instrumental drift. Reference materials (USGS BHVO-2, BCR-2, RGM-2, AVG-2,) were used as quality-control standards.

Bulk-rock REE analysis of sulfide ore

REE analyses of bulk ore were done by an Agilent 7700e ICP-MS at Nanjing FocuMS Technology Co. Ltd, Jiangsu province, China. About 40 mg powder was mixed with 0.5 mL 60 wt. % HNO₃ and 1.0 mL 40 % HF in high-pressure PTFE bombs. To ensure complete digestion, the bombs were steel-jacketed and placed in the oven at 195 °C for 3–4 days. Then the bombs were opened, solutions dried down on a hotplate, re-dissolved with 5 mL 15 wt. % HNO₃ and 1 mL Rh internal standard, sealed and placed in the oven at 150 °C. Aliquots of the digestions were nebulised into an Agilent Technologies 7700x quadrupole ICP-MS to analyse trace elements. Geochemical USGS reference materials for quality control were basalt (BCR-2, BHVO-2), rhyolite (RGM-2), andesite (AVG-2), and granodiorite (GSP-2).

LA-ICP-MS zircon U-Pb dating

SEM imaging and LA-ICP-MS zircon U-Pb dating of zircon was obtained at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, using a TESCAN Integrated Mineral Analyser (TIMA3 GHM) system and an Agilent 7900 ICP-MS coupled with a RESOlution M-50 193-nm ArF Excimer Laser Ablation system, respectively. Based on observations of internal textures, inclusion- and fracture-free zircon grains were selected for U-Pb dating. Each analysis was performed with a uniform spot size diameter of 37 µm at 5 Hz with an energy of 6 J/cm². NIST SRM 610 was analysed once for every six analyses of the tested sample. The reference zircon (GJ-1) was analysed twice for every six analyses as an external standard, and the reference zircon (Plesovice) was analysed once for every six analyses as a control standard to check data reproducibility. More detailed analytical procedures are given in Yuan *et al.* (2004). The U-Pb ages were processed by ICPMSDataCal software (Liu *et al.*, 2008) and the calculation of U-Pb ages was performed by the ISOPLOT 3.0 software package (Ludwig, 2003).



Supplementary Figures









Figure S-2 (a) Reflected-light photomicrograph of hematite in the red sandstone. (b) Transmitted-light photomicrograph of xenotime in the red sandstone. (c) Reflected-light photomicrograph of hematite, xenotime, rutile, and zircon in the red sandstone. (d) SEM-EDS spectral image of apatite-rich beds in the overlying dolostone. (e, f) Reflected-light photomicrographs of anhydrite barite, hematite, and chalcopyrite in the bedded mineralisation. Abbreviations: Anh, anhydrite; Ap, apatite; Bn, bornite; Brt, barite; Ccp, chalcopyrite; Gn, galena; Hem, hematite; Rt, rutile; Qz, quartz; Xtm, xenotime; Zrn, zircon.



Figure S-3 Photographs of sulfide ore samples and μ -XRF images from the bedded orebody (about 10 m thick) at the Yushui deposit. (a) Sampling locations of fourteen bulk ore samples from the bedded orebody. (b) μ -XRF images and HREE concentrations of seven bulk ore samples (Ys01-07) from the lower part of the bedded orebody. Seven bulk ore samples from the lower part of the bedded/massive have high Σ REE and HREE concentrations of 1.1–6.6 × 10⁴ ppm and 1.1–6.1 × 10⁴ ppm, respectively, with a relatively high average HREE concentration of 2.5 × 10⁴ ppm. Seven bulk ore samples from the upper part of bedded/massive mineralisation display relatively low Σ REE and HREE concentrations of 2.6–6.6 × 10³ ppm and 2.3–5.4 × 10³ ppm (Table S-1).





Figure S-4 (a–d) Photomicrographs of (a) iimoriite-[Y], (b) synchysite-[Y], (c) kamphaugite-[Y], and (d) chernovite-[Y] in a matrix of bornite and chalcopyrite. (e–h) Photomicrographs and SEM-EDS spectral image of xenotime in the footwall red sandstone. (e) Anhedral xenotime-I grains intergrown with hematite in a veinlet. (f) SEM-EDS spectral image of anhedral fine-grained xenotime-II grains. (g, h) Euhedral to subhedral xenotime-III grains. Abbreviations: Bn, bornite; Ccp, chalcopyrite; Chv-[Y], chernovite-[Y]; Gn, galena; Hem, hematite; Khg-[Y], kamphaugite-[Y]; Iim-[Y], iimoriite-[Y]; Syn-[Y], synchysite-[Y]; Xtm, xenotime.





Figure S-5 Sketch figure showing sampling locations. Samples of hingganite-[Y] (1804YS04), uraninite (1804YS10), and xenotime-[Y] (1605YS04) were collected from the lower part of the bedded/massive orebody, 14 samples of sulfide bulk ore were collected from the bedded orebody from lower (Ys01) to upper part (Ys14). 16 samples for bulk-rock Nd isotope, 1 sample (20YS28) for detrital zircon U-Pb, and 5 samples (20YS11, 23, 26, 29 and 32) for clastic xenotime U-Pb analyses were taken from the footwall red sandstone.





Figure S-6 Sm-Nd isochron plot of (a) hingganite-[Y] and (b) xenotime from the bedded mineralisation.





Figure S-7 SEM-EDS spectral images of (a) zircon, (b) xenotime, and (c, d) monazite in the red sandstone, showing dissolution-modification textures, and as-yet unidentified HREE-bearing and Al-Si-mix mineral phases within fluid-modified zircon, xenotime, and monazite. Abbreviations: Al-Si-mix, Aluminosilicate mixture; Hem, hematite; HREE, unidentified/unnamed HREE-bearing mineral phases; Mnz, monazite; Rt, rutile; Qz, quartz; Xtm, xenotime; Zrn, zircon.



Supplementary Tables

Table S-1REE contents in bedded sulfide ore samples from the Yushui deposit (in ppm).

Table S-2LA-ICP-MS U-Pb data of xenotime and uraninite in the ore samples. Samples 1804YS04(uraninite) and 1605YS04 (xenotime) are from the lower part of the bedded mineralization.

Table S-3LA-ICP-MS U-Pb data of xenotime-I, -II, and -III from the red sandstone of drillcore (ZK01).

Table S-4LA-ICP-MS U-Pb data of detrital zircon samples from the red sandstone in drillcore (ZK01).Ages older than 1000 Ma were calculated using ²⁰⁷Pb/²⁰⁶Pb ratios, and ages younger than 1000 Ma were calculated using ²⁰⁶Pb/²³⁸U ratios.

Table S-5Sm-Nd isotope data of hingganite-[Y] (1804YS10), xenotime (1605YS04), and lowerCarboniferous red sandstone from the Yushui deposit. Samples 1804YS10 and 1605YS04 are from the lowerpart of the bedded mineralization, and 16 samples of the red sandstone are from drillcore (ZK01).

Tables S-1 through S-5 (.xlsx) are available for download from the online version of this article at <u>https://doi.org/10.7185/geochemlet.2317</u>.



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