

He et al.

Supplementary file: Appendix 1

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He et al.: Magnetite–apatite deposit from Sri Lanka: implications on Kiruna-type mineralization associated with ultramafic intrusion and mantle metasomatism

ANALYTICAL METHODS

The locations of the samples analysed in this study are given in Table 1 and plotted in Fig. 2a. Polished thin sections were prepared from representative samples at the School of Earth and Space Sciences, Peking University. Electron Probe Microanalyses and Backscattered electron (BSE) imaging were carried out using an electron microprobe analyser (JEOL JXA8530F) at the Chemical Analysis Division of the Research Facility Center for Science and Technology, the University of Tsukuba, Japan. The analyses were done using 15 kV accelerating voltage and a 10 nA probe current, and the data were regressed using an oxide-ZAF correction program supplied by JEOL. Representative compositions of minerals are given in Supplementary Table 1.

Representative samples were chosen for whole-rock geochemical analyses which were devoid of surface alteration or weathering. The samples were reduced in a jaw crusher, and then manually fine-powdered in an agate mortar. Whole-rock major-oxides and trace-elements including rare earth elements (REE) of sixteen representative samples were analyzed by XRF and LA–ICP–MS instruments at the National Research Centre of Geoanalyses, Beijing (China). The results are presented in Supplementary Table 2.

Zircon separation involved gravimetric and magnetic techniques from crushed rock samples, followed by hand picking under a binocular microscope at the Yu’neng Geological and Mineral Separation Survey Centre, Langfang city, Hebei Province, China. Individual grains were mounted onto double-sided adhesive tape and enclosed in epoxy resin discs. The discs were polished to expose zircon centres and gold coated for CL imaging and U–Pb isotope analysis. Zircon grains were imaged using cathodoluminescence (CL) to study the morphology and internal structures, and to choose target sites for U–Pb analyses. The CL imaging at the Beijing Geoanalysis Centre used a scanning electron microscope (JSM510) equipped with Gatan CL probe.

U–Pb dating and trace element analysis of zircon were simultaneously conducted by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) at the Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Science, Beijing, China. Laser sampling was performed using a GeolasPro laser ablation system that consists of a New Wave Research UP193FX excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a homogenizing imaging optical system. An Agilent 7500a ICP–MS instrument was used to acquire ion-signal intensities. The ablated samples (ions) were then transported from laser to ICP–MS by helium carrier gas through a 3-mm diameter PVC tube and mixed with high-purity argon gas just before entering the ICP–MS torch. This reduces elemental fractionation of the sample. A spot size of 35 μm with a repetition rate of 8 Hz and spot energy density of 8–10 J/cm² was used

for ablation. This produced about 15 to 20- μm -deep pits within the zircon. A single grain analysis time was 100 s (15 s with laser off, 40 s with laser on, 45 s of delays including background measurement). Raw count rates for ^{29}Si , ^{49}Ti , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{179}Hf , ^{181}Ta , ^{202}Hg , ^{207}Pb , ^{206}Pb , ^{208}Pb , ^{232}Th , and ^{238}U were collected.

Plešovice zircon and NIST610 glass were used as external standards for U–Pb dating and trace element calibration, respectively. Time-dependent drifts of U–Th–Pb isotopic ratios were corrected using a linear interpolation (with time) for every ten analyses. GLITTER 4.0 software (Griffin et al. 2004) was used to perform off-line data reduction and integration of background and analysed signals. Three integration times were used: 30 μs for all four Pb, 6 μs for ^{29}Si , ^{90}Zr , 15 μs for ^{232}Th , ^{238}U and 10 μs for the rest of the isotopes. Final assessment of uncertainty and data visualization were done in Excel™ using Isoplot/Ex_ver4.15 (Ludwig, 2012). Errors are quoted at the 2σ level. Full isotopic data and details of the analytical method without propagation for their systematic uncertainty component, are listed in Supplementary Table 3.

Analyses of Plešovice throughout the study yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 337.1 ± 3.2 Ma ($n = 20$, MSWD = 0.02), within uncertainty of the published $^{206}\text{Pb}/^{238}\text{U}$ age of 337.13 ± 0.37 Ma (ID-TIMS) (Sláma et al. 2008). However, the uncertainties of standards could be overestimated according to the low MSWD of weighted mean age from Plešovice standards. Zircon standard 91500 was treated as an unknown to monitor the stability and accuracy of acquired U–Pb data. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age for 91500 in this study is 1090 ± 10 Ma, $n = 10$, MSWD = 2.7, which is slightly outside uncertainty of the published value of Wiedenbeck et al. (1995). Validation results from 91500 (without propagation for systematic uncertainties) highlighting the need for an additional variance component (1.8% 2σ). Propagating this systematic, excess variance uncertainty into the weighted mean uncertainty of the sample result, follows Horstwood et al. (2016).

In situ zircon Hf isotopic analyses were conducted on the same spots or in the adjacent domains where U–Pb dating was done. The energy density of 15–20 J/cm^2 and a spot size of 45 μm were used. The flattest, most stable portions of the signal were selected for analysis. Adjustment for the isobaric interference of ^{176}Yb on ^{176}Hf was performed in ‘real time’ as advocated by Woodhead et al. (2005), which involved measuring the interference-free ^{172}Yb and ^{173}Yb during the analysis, calculating mean βYb values from ^{172}Yb and ^{173}Yb and using the $^{176}\text{Yb}/^{172}\text{Yb}$ ratio of 0.5886 (Chu et al. 2002). Zircon 91500 was used as the reference standard with a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282306 ± 10 (Woodhead et al. 2005). All the Lu–Hf isotope analysis results were reported with an error of 1σ . The decay constant of ^{176}Lu of 1.865×10^{-11} year^{-1} was adopted (Scherer 2001; Söderlund et al. 2004). Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios $\text{Hf}(t)$ were calculated with reference to the chondritic reservoir (CHUR) of (Blichert-Toft and Albarede, 1997) at the time of zircon growth from the magma. Single-stage Hf model age (T_{DM}) was calculated with respect to the depleted mantle with present-day $^{176}\text{Lu}/^{177}\text{Hf} = 0.28325$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ (Griffin et al. 2000). Two-stage Hf model age ($2s T_{\text{DM}}$) was calculated with respect to the average continental crust with a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.015 (Griffin et al. 2004). The results are presented in Table 2.

RESULTS

Mineral chemistry

Amphibole. Amphibole in all the studied samples is characterized by high Ca and (Na + K) contents (1.80–1.97 pfu and 0.56–0.98 pfu, respectively), and shows compositional variation depending on its microstructural occurrence (Supplementary Table 1; Fig. 5a).

Amphibole from ultramafic host sample VC18-4 and VC16-1 is classified as ferropargasite, $X_{\text{Mg}} < 0.5$ and shows the highest total Fe content ($\text{Fe}^{2+} + \text{Fe}^{3+} = 2.7\text{--}3.1$ pfu). Amphiboles from two ultramafic host samples show similar composition with $X_{\text{Mg}} = 0.38\text{--}0.47$ ($X_{\text{Mg}} = \text{Mg}/(\text{Fe}^{2+} + \text{Mg})$), and plot in the ferropargasite field (Fig. 5a) according to Leake et al. (1997) classification.

Calcic amphibole in massive magnetite ore sample VC18-3 shows the largest compositional variation, and can be classified as pargasite, edenite and actinolite suggesting three different stages of formation. The brown colored edenite is Fe-rich ($\text{Fe}^{\text{T}} = 1.9\text{--}2.1$ pfu) with $X_{\text{Mg}} = 0.55\text{--}0.63$, whereas the greenish pargasite is Na-rich with lower Fe content ($\text{Fe}^{\text{T}} = 1.4\text{--}1.5$ pfu). Late-stage actinolite is Si-rich (6.6–7.5 pfu) with the lowest Fe content ($\text{Fe}^{\text{T}} = 0.7\text{--}1.0$ pfu) with notably higher X_{Mg} in the range of 0.82–0.87. Actinolite also shows the highest Ca content (1.95–1.96 pfu) and low (Na + K) content (0.20–0.24 pfu). No compositional variations are observed between cores and rims in individual grains.

Amphiboles from disseminated ore rocks sample VC18-6 are classified as pargasite and ferropargasite, and the tiny irregular amphibole inclusions have higher X_{Mg} value (0.58) classifying as ferropargasite (Fig. 5a). The amphibole layer between clinopyroxene and magnetite has lower X_{Mg} value (0.42–0.46).

Amphiboles from transitional zone rocks VC16-3 and VC18-5 fall cross the fields of pargasite and ferropargasite in Fig. 5a, with a similar X_{Mg} value (0.40–0.55) and varied Fe content ($\text{Fe}^{\text{T}} = 0.7\text{--}1.0$ pfu).

Clinopyroxene. Clinopyroxene in all samples is calcic Mg-rich ($X_{\text{Mg}} = \text{Mg}/(\text{Fe} + \text{Mg}) = 0.60\text{--}0.80$), classified as diopside (Fig. 5b) according to Morimoto (1988), although the X_{Mg} varies among different samples. Clinopyroxene in massive ore samples VC18-3 and disseminated ore sample VC18-6 shows slightly higher X_{Mg} of 0.64–0.80 than in the ultramafic host rock (samples VC16-1 and VC18-4, $X_{\text{Mg}} = 0.60\text{--}0.64$) and that in the transitional boundary rock (samples VC16-3 and VC18-5, $X_{\text{Mg}} = 0.62\text{--}0.65$). The clinopyroxene shows low Na_2O content (< 1.0 wt% Na_2O) and Fe content (6.3–10.1 wt% FeO) and high Mg content (11.9–14.8 wt% MgO), especially near actinolite, which has very low Fe and high Mg contents.

Clinopyroxene in massive ore sample VC18-4 shows the lowest Fe content (12.1–12.3 wt% FeO) and highest Mg content (10.4–10.7 wt% MgO), and those in the other two samples (sample VC18-5 and VC18-6) have values in between. No compositional variations are noticed between cores and rims in individual grains. All clinopyroxene crystals show uniform Ca content with CaO varies from 22 to 24 wt%.

Apatite. Two textures of apatite can be identified based on microstructural features. The first is coarse (1–3 mm) euhedral grains with no fluid inclusions occurring with magnetite. The second type is represented by fine-grained apatite and shows abundant fluid-inclusions, the occurrence of which is restricted to veinlets in silicate minerals, together with scapolite, or as needle-like inclusions in scapolite, the latter two possibly belonging to the same generation. All the analyzed apatite compositions correspond to chlor-fluorapatite. Halogen contents of apatite are 1.86–2.15 wt% F and 1.91–2.29 wt% Cl for massive ore sample VC18-3, 1.92–2.25 wt% F and 1.73–2.14 wt% Cl for disseminated ore sample VC18-6, 2.28–2.53 wt% F and 1.68–2.11 wt% Cl for transitional zone sample VC16-3, and 2.66–3.04 wt% F and 0.99–1.15 wt% Cl for host ultramafic sample VC16-1. Apatite in transitional zone sample VC18-5 shows the highest fluorine and the lowest chlorine contents of 2.87–3.20 wt% F and 0.80–1.07 wt% Cl. Whereas apatite in massive ore sample VC18-3 shows the highest chlorine and the lowest fluorine contents of 1.81–2.29 wt% F and 0.27–0.33 wt% Cl (Fig. 5c). Overall, the fluorine content and chlorine content in apatite shows a negative correlation, and the chlorine content increases with the increasing Fe content from host rocks to massive ore rocks.

Magnetite. The two major textures of magnetite (massive and disseminated) analysed by XRF on both host rocks and ore samples are dominantly characterised by a near end-member compositions, and have very low Ti content. No hematite or ilmenite exsolution has been detected under back scattered image. The MgO content is also very low (<0.3 wt%). The massive type euhedral magnetite shows higher MgO content than the disseminated ore magnetite, although the Mg-rich spinel exsolution is largely found in the massive magnetite ore samples. The major element composition of magnetite is nearly constant in the studied rocks. The Ni and Cr contents are also considerably low in both generations but higher in ore rocks than in the host rocks (Fig. 5d; Supplementary Table 1).

Scapolite. Scapolite in the studied sample is generally characterized by high CaO (> 12 wt%), and moderate to low Na₂O (4.87–5.97 wt%) and moderate chlorine (1.27–1.56 wt%) contents (Supplementary Table 1). The meionite end member (*Me*) is in the range of 51–58 ($Me = 100 \times (Ca + Mg + Fe + Mn + Ti) / (Na + K + Ca + Mg + Fe + Mn + Ti)$). Scapolite inclusions in magnetite shows no compositional variance compared to those in the matrix. Compared to apatite, the scapolite has very little fluorine content (<0.05 wt% F).

Spinel. Spinel occurs as rounded grains in the grain boundary and cleavages of magnetite or as euhedral inclusions within magnetite (Fig. 4c, d, f). They are characterized by high Al₂O₃ (59.9–63.7 wt%), relatively high total FeO (18.3–20.9 wt%) and MgO (13.0–14.3 wt%), with less ZnO (3.4–3.9 wt%) and very low Cr₂O₃ content (<0.1 wt%). The X_{Mg} ($X_{Mg} = Mg^{2+} / (Mg^{2+} + Fe^{2+})$) is 0.55–0.62 and the Mg: Fe²⁺ ratio is 1.2–1.6. Individual grains do not show any compositional zoning from core to rim.

Geochemistry

Whole rock geochemical data, including major, minor, trace and rare earth elements on two ultramafic host rocks (VC16/1 and 18/4), four transitional zone samples (VC16/3, 16/5, 16/6 and 18/5) and one disseminated ore sample (VC16/2) are given in Supplementary Table 2. The massive ore sample was not analyzed for geochemistry due to the very high proportion of magnetite. All the analyzed samples show low LOI content (0.11–1.05).

The major element characteristics for all analyzed samples include low SiO₂ content (39–

48 wt%), highly variable FeO (7.8–11.6 wt%) and Fe₂O₃ (4.9–13.0 wt%) content, with moderate Mg# (=molar Mg/(Mg + Fe²⁺_{total})) in the range of 37–57. The rocks show variable P₂O₅ content ranging from 0.25 to 3.45 wt% with very high CaO content (15–20 wt%). The TiO₂ content of the iron oxide samples ranges from 0.1–0.38 wt%, and has an overall low total alkali (Na₂O+K₂O) content of 0.9–2.4 wt%.

In terms of mantle rock forming elements (MRFE), all the studied samples display overall depletion in Ni and Cr concentrations compared to average MORB, with very low Cr content of 2–17 ppm. However, they are also characterized by varied Cu concentrations (142–4521 ppm), high Zn (125–209 ppm) and Co (73–108 ppm) contents. Incompatible trace element abundances show enrichment in Sr but depletions in Rb and Ba. All studied samples show relative depletion in high field strength elements (HFSE; Zr, Hf, Ti, Y, Pb, Supplementary Table 2), low U (0.5–3.5 ppm) and varied Th (2.4–68.4 ppm) contents. All studied samples shows high Zr content (135–372 ppm).

In terms of rare earth elements (REE), the samples show distinct light REE (LREE) and medium REE (MREE) enrichment over heavy REE (HREE), with moderate LREE/MREE and steep LREE/HREE fractionation trends [(La/Sm)_N = 0.7–1.9 and (La/Yb)_N = 6.2–29.2] (Fig. 6a). The LREE shows larger variation with an increasing trend of LREE from the ultramafic host sample (VC16-1) to disseminated ore sample (VC16-2) associated with increasing modal apatite proportion. The Nd_N shows the highest values as indicated by convex REE patterns (Fig. 6a). The HREE shows tight and consistent patterns [(Gd/Yb)_N = 4.5–6.7, (Dy/Yb)_N = 1.61–2.32] and document moderate to strong MREE/HREE fractionation. In all the studied samples, the absence of a significant Eu anomaly indicates the lack of significant feldspar fractionation before emplacement. The primitive-mantle-normalized trace element patterns for the studied samples (Fig. 6b) exhibit pronounced positive anomalies of Th, Ba, Sm, variable anomalies of Nb, Ta and P, and negative anomalies of Zr–Hf and Ti. The overall low (Nb/Th)_{PM} ratios (0.06–1.53)

Geochronology

Sample VC16-3. Zircon grains from the transition zone sample VC16-3 are mostly anhedral, with irregular morphology. They are colorless to light brown in color, transparent to translucent, and mostly range in length from 100–200 µm. Two types of zircon grain are identified by CL imaging (Fig. 7), based on their internal morphology. Most of the zircon population is homogeneous without cores and rims texture. The remaining grains show complex and heterogeneous internal structure. A total of 30 analyses were made on homogeneous zircon grains using LA–ICP–MS. The Th and U values show variable contents in the range of 31 to 272 ppm and 22 to 194 ppm respectively, with high Th/U values in the range of 0.44 to 2.04. Most of the values are higher than 1.0, suggesting that these grains are magmatic in origin (Supplementary Table 3). Excluding 3 analysis with low signal (spots 21, 22, 29) and 5 analyses (spots 2, 3, 20, 24, 30) which are discordant (> 5% discordance), 22 analyses form a coherent group within analytical error and a Gaussian-style distribution pattern with one major age peak (Fig. 8a). The weighted mean ²⁰⁶Pb/²³⁸U age with and without propagation for their systematic uncertainty component is 527.2 ± 3.1/10.0 Ma (MSWD = 2.2, n = 22) (Fig. 8b).

Sample VC18-4. Sample VC18-4 from the ultramafic host rock yielded sufficient number of zircon grains for analysis. Zircon grains from this sample are mostly colorless or light brown. They show elliptical morphology with length varying from 50 to 250 μm and a length to width ratio of 1:1 to 2:1. In CL images (Fig. 7), some grains display core-rim textures. Many grains have chaotically structured cores, with few cores showing clear magmatic oscillatory zoning suggesting an igneous origin. A total of 30 analyses on both core and rim domains from 27 zircon grains were obtained. The Th and U contents show variable contents ranging from 38 to 153 ppm and 39 to 449 ppm respectively (Supplementary Table 2). The Th/U ratios show a wide range from 0.08 to 1.31. Most of the values are higher than 0.6. Five analysis (spot 7, 14, 15, 21, 26) has >5% discordance, and four analyses yield older ages (701–546 Ma) which do not form a coherent group with other zircon ages, the rest of 19 analyses form one age group within analytical error (Fig. 8c). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of this group with and without propagation for their systematic uncertainty component is $529.8 \pm 3.7/10.2$ Ma (MSWD = 2.5, $n = 19$) (Fig. 8d).

Lu–Hf isotopes

Sample VC16-3. Six zircon grains from sample VC16-3 were analyzed for their in situ Lu–Hf isotopic composition, and the results show tight ($^{176}\text{Hf}/^{177}\text{Hf}$)_i range of 0.282337 to 0.282396 (Table 2). The $\epsilon\text{Hf}(t)$ values are in the range of -3.7 to -1.5, with two-stage Hf model ages ($2s\ T_{\text{DM}}$) of 1591 to 1726 Ma.

Sample VC18-4. Five zircon grains from sample VC18-4 were analyzed for their in situ Lu–Hf isotopic composition. The results show tight ($^{176}\text{Hf}/^{177}\text{Hf}$)_i range of 0.282405 to 0.282481 (Table 2). The $\epsilon\text{Hf}(t)$ values are in the range of -1.6 to -1.6, plotted close to the CHUR line in Fig. 9, with two-stage Hf model ages ($2s\ T_{\text{DM}}$) of 1399 to 1583 Ma.

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