# Copper Endowment of the Magmatic Rocks from Eastern Sakarya Zone (Türkiye): Insights from Zircon and Apatite Geochemical Evolution

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## APPENDIX A

This section includes descriptions of the analytical methods we have used in this study.

### 1. Electron microprobe analysis

The geochemical composition of apatite from Güzel-Yayla rocks was analyzed using a JEOL JXA-8230 Superprobe electron microprobe (-EPMA) at Wuhan SampleSolution Analytical Technology Co., Ltd., in Wuhan, China, utilizing a 5-micron spot size, a $1*10^{-8}$ A beam current, and a 15 keV accelerating voltage. The geochemical composition of apatite grains is presented in Table S3. The standards used for EPMA analysis of apatite grains in this study are listed in Table S3.

### 2. Whole rock major element analysis

The sample pre-treatment of whole rock major element analysis was made by the fusion method at Wuhan SampleSolution Analytical Technology Co., Ltd., in Wuhan, China. The flux was a mixture of lithium tetraborate, lithium metaborate, and lithium fluoride (45:10:5). Ammonium nitrate and lithium bromide were used as oxidant and release agents, respectively. The fusion temperature was 1050°C, and the melting time was 15 minutes.

A Zsx Primus II wavelength dispersive X-ray fluorescence spectrometer (XRF) produced by RIGAKU, Japan, was used for the analysis of the whole rock major elements. The X-ray tube is a 4.0 kW end-window Rh target. The test conditions were voltage: 50 kV, and current: 60 mA. All major element analysis lines are kα. The standard curve uses the national standard material, with rock standard sample: GBW07103: granite standard sample, GBW07104: andesite standard sample, GBW07105: basalt standard sample and GBW07111: granodiorite standard sample. The data were corrected by the theoretical α coefficient method. The analytical precision is better than 1% for elements > 1 wt% and ~5% for elements < 1 wt% (e.g., P2O5). The major-element compositions of magmatic rocks are presented in Table S1.

### 3. Whole rock trace element analysis

Trace element analysis of whole-rock samples was conducted on an Agilent 7700e ICP-MS at Wuhan SampleSolution Analytical Technology Co., Ltd., in Wuhan, China. The detailed sample-digesting procedure was as follows: (1) Sample powder (200 mesh) was located in an oven at 105°C for drying for 12 hours; (2) 50 mg of sample powder was accurately weighed and placed in a Teflon bomb; (3) 1 ml of HNO3 and 1 ml of HF were slowly added into the Teflon bomb; (4) The Teflon bomb was retained in a stainless steel pressure jacket and heated to 190°C in an oven for over 24 hours; (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140°C and evaporated to incipient dryness, then 1 ml of HNO3 was added and evaporated to dryness again; (6) 1 ml of HNO3, 1 ml of MQ water, and 1 ml of an internal standard solution (1 μg/g In) were added, and the Teflon bomb was resealed and placed in the oven at 190°C for over 12 hours; (7)

The final solution was transferred to a polyethylene bottle and diluted to 100 g by the addition of 2% HNO3. The trace element compositions of the magmatic rocks are presented in Table S1. International standards BHVO-2, BCR-2, RGM-2, and JA-2 were used during the analysis of our samples, and both the analytical results and the recommended reference values are also provided in Table S1.

**4. Sr Isotope Ratio Analyses Using MC-ICP-MS**

Sample Digestion: (1) Sample powders (200 mesh) were placed in an oven at 105°C for drying for 12 hours. (2) 50-200 mg sample powders were accurately weighed and placed in a Teflon bomb. (3) 1-3 ml HNO3 and 1-3 ml HF were added to the Teflon bomb. (4) The Teflon bomb was put in a stainless-steel pressure jacket and heated to 190°C in an oven for over 24 hours. (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140°C and evaporated to incipient dryness, then 1 ml HNO3 was added and evaporated to dryness again. (6) The samples were dissolved in 1.5 mL of 2.5 M HCl.

Column Chemistry: After centrifugation, the supernatant solutions were loaded into an ion exchange column packed with AG50W resin. Columns were rinsed with 2.5 M HCl to remove undesirable matrix elements. Finally, the Sr fractions were eluted using 2.5 M HCl and gently evaporated to dryness before mass-spectrometric measurement. The residues were rinsed with 10 mL of 4.0 M HCl, and then the REE fractions were eluted using 10 ml of 4.0 M HCl. The REE solutions were used to separate the Nd fraction by the Nd-column method.

The Sr fractions were separated again by the Sr-specific resin. The solutions were first converted to the HNO3 media (3 M HNO3). Then, the solutions were loaded into the Sr-specific resin and pre-conditioned with 6 M HCl and 3 M HNO3. Columns were rinsed with 3 M HNO3 to remove undesirable matrix elements. Finally, Sr was eluted using MQ H2O and gently evaporated to dryness before mass-spectrometric measurement.

Sr isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus, a double-focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with $10^{11}$ Ω resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor $^{83}Kr^{+1}$, $^{167}Er^{+2}$, $^{84}Sr^{+1}$, $^{85}Rb^{+1}$, $^{86}Sr^{+1}$, $^{173}Yb^{+2}$, $^{87}Sr^{+1}$, and $^{88}Sr^{+1}$. The large dry interface pump (120 $m^3$ $hr^{-1}$ pumping speed), newly designed H skimmer cone, and the standard sample cone were used to increase instrumental sensitivity. Sr single-element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard solution of 200 μg $L^{-1}$ NIST SRM 987 was used regularly to evaluate reproducibility and accuracy. Typically, the signal intensities of $^{88}Sr$ in NIST 987 were > ~7.0 V. Sr isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 s integration time per cycle). The total time of one measurement lasted about 7 minutes.

The exponential law, initially developed for the TIMS measurement (Russell et al. 1978) and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess instrumental mass discrimination. Mass discrimination correction was carried out via internal normalization to an $^{88}Sr/^{86}Sr$ ratio of 8.375209 (Lin et al. 2016). Interference elements Ca, Rb, Er, and Yb were completely separated by the exchange resin process. The remaining interferences of $^{83}Kr^{+1}$, $^{85}Rb^{+1}$, $^{167}Er^{+2}$, and $^{173}Yb^{+2}$ were corrected based on the method described by (Lin et al. 2016). One international NIST 987 standard was measured for every seven samples analyzed. All data reduction for the MC-ICP-MS analysis of Sr isotope ratios was conducted using the "Iso-Compass" software (Zhang et al. 2020). Analyses of the NIST 987 standard solution yielded an $^{87}Sr/^{86}Sr$ ratio of 0.710242±14 (2SD, n=345), which is identical within error to their published values of 0.710248 ±12 (Zhang et al. 2020). In addition, the USGS reference materials JB-3 (basalt) and RGM-2 (rhyolite) yielded results of 0.703406 ± 0.000008 (2SD, n=63) and 0.704152 ± 0.000007 (2SD, n=20) for $^{87}Sr/^{86}Sr$, respectively, which is identical within error to their published values (Li et al. 2012; Zhang

and Hu 2020). The Sr isotopic compositions of the magmatic rocks, along with the standards used in this study, are provided in Table S1.

**5. Whole rock Nd isotope ratio analyses using MC-ICP-MS**

Column Chemistry: The REE solution from the Sr-column method was evaporated to incipient dryness and taken up with 0.18 M HCl. The converted REE solution was loaded into an ion-exchange column packed with LN resin. After complete draining of the sample solution, columns were rinsed with 0.18 M HCl to remove undesirable matrix elements. Finally, the Nd fraction was eluted using 0.3 M HCl and gently evaporated to dryness before mass-spectrometric measurement.

Nd isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus, a double-focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with $10^{11}$ Ω resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H4 to monitor $^{142}Nd^{+1}$, $^{143}Nd^{+1}$, $^{144}Nd^{+1}$, $^{145}Nd^{+1}$, $^{146}Nd^{+1}$, $^{147}Sm^{+1}$, $^{148}Nd^{+1}$, $^{149}Sm^{+1}$, and $^{150}Nd^{+1}$. The large dry interface pump (120 $m^3$ $hr^{-1}$ pumping speed), newly designed H skimmer cone, and the standard sample cone were used to increase instrumental sensitivity. Nd single-element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the standard solution of 200 μg $L^{-1}$ GSB 04-3258-2015 was used regularly to evaluate reproducibility and accuracy. Typically, the signal intensities of $^{142}Nd^{+1}$ in GSB 04-3258-2015 were > ~2.5 V. Nd isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 seconds integration time per cycle). The total time of one measurement lasted about 7 min. The exponential law, initially developed for the TIMS measurement (Russell et al. 1978) and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess instrumental mass discrimination. Mass discrimination correction was carried out via internal normalization to a $^{146}Nd/^{144}Nd$ ratio of 0.7219 (Lin et al. 2016). The interference element Sm was completely separated by the exchange resin process. The remaining interference of $^{144}Sm^{+1}$ was corrected based on the method described by (Lin et al. 2016). All data reduction for the MC-ICP-MS analysis of Nd isotope ratios was conducted using the "Iso-Compass" software (Zhang et al. 2020). One GSB 04-3258-2015 standard was measured for every seven samples analyzed. Analyses of the GSB 04-3258-2015 standard yielded a $^{143}Nd/^{144}Nd$ ratio of 0.512440±6 (2SD, n=31), which is identical within error to their published values (0.512438±6 (2SD) (Li et al. 2017)). In addition, the USGS reference materials JB-3 (basalt) and RGM-2 (rhyolite) yielded results of 0.513066±0.000007 (2SD, n=82) and 0.512801±0.000007 (2SD, n=80) for $^{143}Nd/^{144}Nd$, respectively, which is identical within error to their published values (Li et al. 2012). The Nd isotopic compositions of the magmatic rocks, along with the standards used in this study, are provided in Table S1.

**6. Pb Isotope Ratio Analyses Using MC-ICP-MS**

Sample Digestion: (1) Sample powders (200 mesh) were placed in an oven at 105°C for drying for 12 hours. (2) 50-200 mg sample powders were accurately weighed and placed in a Teflon bomb. (3) 1-3 ml HNO3 and 1-3 ml HF were added to the Teflon bomb. (4) The Teflon bomb was put in a stainless-steel pressure jacket and heated to 190°C in an oven for over 24 hours. (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140°C and evaporated to incipient dryness, then 1 ml HNO3 was added and evaporated to dryness again. (6) The samples were dissolved in 1.0 mL of 1.0 M HBr.

Column Chemistry: After centrifugation, the supernatant solution was loaded into an ion exchange column packed with AG resin. Columns were rinsed with 1.0 M HBr to remove undesirable matrix elements. Finally, the Pb fraction was eluted using 6.0 M HCl and gently evaporated to dryness before mass-spectrometric measurement.

Pb isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus, a double-focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with $10^{11}$ Ω resistors. The Faraday collector configuration of the mass system was composed of an array to monitor $^{204}$(Pb+Hg), $^{206}$Pb, $^{207}$Pb, $^{208}$Pb, $^{203}$Tl, $^{205}$Tl, and $^{202}$Hg. The large dry interface pump (120 $m^3$ $hr^{-1}$ pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase instrumental sensitivity. Pb single-element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard solution of 100 μg $L^{-1}$ NIST 981 was used regularly to evaluate reproducibility and accuracy. Typically, the signal intensities of $^{208}Pb^{+1}$ in NIST 981 were > ~6.0 V. Pb isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 seconds integration time per cycle). The total time of one measurement lasted about 7 min.

The exponential law, initially developed for the TIMS measurement (Russell et al. 1978) and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess instrumental mass discrimination in this study. Mass discrimination correction was carried out via normalization to a $^{205}Tl/^{203}Tl$ ratio of 2.38714 (the certified value of NIST SRM 997). All data reduction for the MC-ICP-MS analysis of Pb isotope ratios was conducted using the "Iso-Compass" software (Zhang et al. 2020). Because of the difference in the mass bias behaviors between Pb and Tl, all measured $^{20x}Pb/^{204}Pb$ ratios of unknown samples were normalized to the well-accepted NIST 981 values of $^{208}Pb/^{204}Pb$ = 36.7262±31, $^{207}Pb/^{204}Pb$=15.5000±13, $^{206}Pb/^{204}Pb$=16.9416±13 (n=119, (Baker et al. 2004)). One NIST 981 standard was measured for every ten samples analyzed. Analyses of the NIST 981 standard yielded external precisions of 0.03% (2RSD) for $^{20x}Pb/^{204}Pb$ ratios. In addition, the USGS reference material JB-3 (basalt) yielded results of $^{208}Pb/^{204}Pb$=38.247±0.002, $^{207}Pb/^{204}Pb$=15.536±0.001, $^{206}Pb/^{204}Pb$=18.293±0.001 (2SD, n=22), respectively, which is identical within error of 0.03% to their published values (Zhang and Hu 2020). The USGS standard reference of RGM-2 (rhyolite) yielded results of $^{208}Pb/^{204}Pb$=38.670±0.002, $^{207}Pb/^{204}Pb$=15.621±0.001, $^{206}Pb/^{204}Pb$=18.961±0.001 (2SD, n=12). The Pb isotopic compositions of the magmatic rocks, along with the standards used in this study, are provided in Table S1.

**7. Whole rock Hf isotope ratio analyses using MC-ICP-MS**

Sample Digestion: (1) Sample powder (200 mesh) was placed in an oven at 105°C for drying for 12 hours. (2) 50-200 mg sample powder was accurately weighed and placed in a Teflon bomb. (3) 1-3 ml HNO3 and 1-3 ml HF were added to the Teflon bomb. (4) The Teflon bomb was put in a stainless-steel pressure jacket and heated to 190°C in an oven for over 24 hours. (5) After cooling, the Teflon bomb was opened and placed on a hot plate at 140°C and evaporated to incipient dryness, then 1 ml HNO3 was added and evaporated to dryness again. (6) The sample was dissolved in 2.0 M HF.

Column Chemistry: After centrifugation, the supernatant solution was loaded into an ion exchange column packed with LN-Spec resin. After complete draining of the sample solution, columns were rinsed with 3 M HCl, 6 M HCl, and 4 M HCl+H2O2 (0.5%) to remove undesirable matrix elements. Finally, the Hf fraction was eluted using 2.0 M HCl and gently evaporated to dryness before mass-spectrometric measurement.

Hf isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus, a double-focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with $10^{11}$ Ω resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H4 to monitor $^{172}Yb^{+1}$, $^{174}Hf^{+1}$, $^{175}Lu^{+1}$, $^{176}Hf^{+1}$, $^{177}Hf^{+1}$, $^{178}Hf^{+1}$, $^{179}Hf^{+1}$, $^{180}Hf^{+1}$. The large dry interface pump (120 $m^3$ $hr^{-1}$ pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase instrumental sensitivity. Hf single-element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard

solution of 100 μg $L^{-1}$ JMC 475 was used regularly to evaluate the instrument's reproducibility and accuracy. The Hf isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 s integration time per cycle). The total time of one measurement lasted about 7 min.

The exponential law, initially developed for the TIMS measurement (Russell et al. 1978) and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess instrumental mass discrimination in this study. Mass discrimination correction was carried out via internal normalization to a $^{179}Hf/^{177}Hf$ ratio of 0.7325 (Lin et al. 2016). The interference elements Yb and Lu have been completely separated by the exchange resin process. The remaining interferences of $^{176}Yb^{+1}$ and $^{176}Lu^{+1}$ were corrected based on the method described by (Lin et al. 2016). One Alfa Hf standard was measured for every seven samples analyzed. All data reduction for the MC-ICP-MS analysis of Hf isotope ratios was conducted using the "Iso-Compass" software (Zhang et al. 2020). Analyses of the JMC 475 standard yielded a $^{176}Hf/^{177}Hf$ ratio of 0.282154±5 (2SD, n=67), which is identical within error to their published values (0.282157±16, (Zhang and Hu 2020)). In addition, the USGS reference materials JB-3 (basalt) yielded results of 0.283215±0.000007 (2SD, n=19) for $^{176}Hf/^{177}Hf$, respectively, which is identical within error to their published values (Zhang and Hu 2020). The Hf isotopic compositions of magmatic rocks are presented in Table S1.

**8. Zircon cathodoluminescence images**

Zircon CL images were obtained at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China, using an Analytical Scanning Electron Microscope (JSM–IT100) connected to a GATAN MINICL system. The imaging condition was 10.0–13.0 kV voltage of the electric field and 80–85 μA current of the tungsten filament.

**9. In-situ U-Pb dating of zircon by LA-ICP-MS**

U-Pb dating and trace element analysis of zircon were simultaneously conducted by LA-ICP-MS at Wuhan SampleSolution Analytical Technology Co., Ltd., in Wuhan, China. Detailed operating conditions for the laser ablation system and the ICP-MS instrument, as well as data reduction, are the same as described by (Zong et al. 2017). Laser sampling was performed using a GeolasPro laser ablation system consisting of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. Helium served as a carrier gas, while argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. A "wire" signal smoothing device is included in this laser ablation system (Hu et al. 2015). The spot size and frequency of the laser were set to 32 μm and 5 Hz, respectively, in this study. Zircon standard Tanz and glass NIST610 were used as internal standards for U-Pb dating (and trace element) calibration, respectively. Each analysis incorporated a background acquisition of approximately 20-30 seconds followed by 50 seconds of data acquisition from the sample. An Excel-based software, ICPMSDataCal, was used to perform offline selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration for trace element analysis and U-Pb dating (Liu et al. 2010; Liu et al. 2008).

The external standards, zircons GJ-1, Plešovice and Tanz, gave mean $^{206}Pb/^{238}U$ ages of 601.5±1.2 Ma (MSWD=1.1), 337.7±0.76 Ma (MSWD=1.5) and 565.4±1.4 Ma (MSWD=0.08), respectively (Table S2), which are similar to the recommended $^{206}Pb/^{238}U$ ages of 601.4±3.0Ma, 337.13 ± 0.37 Ma, 566.16 ± 0.77 Ma, respectively (Hu et al. 2021; LUAN et al. 2019; Sláma et al. 2008). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 (Ludwig 2003). The zircon U-Pb ages of the magmatic rocks, along with the U-Pb results of the standards, are presented in Table S2.

**10. In-situ trace element analysis of zircon and apatite by LA-ICP-MS**

Trace element analysis of zircon and apatite was conducted by LA-ICP-MS at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for

the laser ablation system and the ICP-MS instrument and data reduction are the same as described by (Zong et al. 2017). Laser sampling was performed using a GeolasPro laser ablation system consisting of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas, and argon was used as the make-up gas mixed with the carrier gas via a T-connector before entering the ICP. A "wire" signal smoothing device is included in this laser ablation system (Hu et al. 2015). The spot size and frequency of the laser were set to 32 μm and 5 Hz for zircon and 44 μm and 5 Hz for apatite. Trace element compositions of zircon were calibrated using the reference materials GJ-1, Plešovice, and Tanz, while apatite was calibrated against various standards (e.g., BHVO-2G, BCR-2G, and BIR-1G) without the use of an internal standard (Liu et al. 2008). Each analysis incorporated a background acquisition of approximately 20-30 seconds followed by 50 seconds of data acquisition from the sample. An Excel-based software, ICPMSDataCal, was used to perform off-line selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration for trace element analysis (Liu et al. 2008). The trace element compositions of zircon and apatite from the ESZ magmatic rocks, along with the results for the standards used, are presented in Tables S2 and S3, respectively.

**11. In-situ Hf isotope analysis of zircon by LA-MC-ICP-MS**

Experiments of in-situ Hf isotope ratio analysis was conducted using a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) in combination with a Geolas HD excimer ArF laser ablation system (Coherent, Göttingen, Germany) hosted at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. A "wire" signal smoothing device is included in this laser ablation system, which produces smooth signals even at very low laser repetition rates down to 1 Hz (Hu et al. 2015). Helium was used as the carrier gas within the ablation cell and was merged with argon (makeup gas) after the ablation cell. Small amounts of nitrogen were added to the argon makeup gas flow to improve the sensitivity of the Hf isotopes (Hu et al. 2012). Compared to the standard arrangement, the addition of nitrogen in combination with the use of the newly designed X skimmer cone and Jet sample cone in Neptune Plus improved the signal intensity of Hf, Yb, and Lu by a factor of 5.3, 4.0, and 2.4, respectively. All data were acquired on zircon in single-spot ablation mode with a spot size of 44 μm. The energy density of laser ablation used in this study was ~7.0 J $cm^{-2}$. Each measurement consisted of 20 seconds of acquiring the background signal followed by 50 seconds of ablation signal acquisition. Detailed operating conditions for the laser ablation system and the MC-ICP-MS instrument and analytical method are the same as described by (Hu et al. 2012). The major limitation to accurate in-situ zircon Hf isotope determination by LA-MC-ICP-MS is the very large isobaric interference from $^{176}Yb$ and, to a much lesser extent, $^{176}Lu$ on $^{176}Hf$. It has been shown that the mass fractionation of Yb (βYb) is not constant over time and that the βYb obtained from the introduction of solutions is unsuitable for in-situ zircon measurements (Woodhead et al. 2004). The under- or over-estimation of the βYb value would undoubtedly affect the accurate correction of $^{176}Yb$ and thus the determined $^{176}Hf/^{177}Hf$ ratio. We applied the directly obtained βYb value from the zircon sample itself in real-time in this study. The $^{179}Hf/^{177}Hf$ and $^{173}Yb/^{171}Yb$ ratios were used to calculate the mass bias of Hf (βHf) and Yb (βYb), which were normalized to $^{179}Hf/^{177}Hf = 0.7325$ and $^{173}Yb/^{171}Yb = 1.132685$ (Fisher et al. 2014) using an exponential correction for mass bias. The interference of $^{176}Yb$ on $^{176}Hf$ was corrected by measuring the interference-free $^{173}Yb$ isotope and using $^{176}Yb/^{173}Yb = 0.79639$ (Fisher et al. 2014) to calculate $^{176}Yb/^{177}Hf$. Similarly, the relatively minor interference of $^{176}Lu$ on $^{176}Hf$ was corrected by measuring the intensity of the interference-free $^{175}Lu$ isotope and using the recommended $^{176}Lu/^{175}Lu = 0.02656$ (Blichert-Toft et al. 1997) to calculate $^{176}Lu/^{177}Hf$. We used the mass bias of Yb (βYb) to calculate the mass fractionation of Lu because of their similar physicochemical properties. Off-line selection and integration of analyte signals, and mass bias calibrations were performed using ICPMSDataCal (Liu et al. 2010).

To ensure the reliability of the analysis data, three international zircon standards of Plešovice, 91500, and GJ-1 were analyzed simultaneously with the actual samples. Plešovice is used for external standard calibration to further optimize the analysis and test results. 91500 and GJ-1 are used as the second standard to monitor the quality of data correction. The external precision (2SD) of Plešovice, 91500, and GJ-1 is better than 0.000020. The test value is consistent with the recommended value within the error range. At the same time, to monitor the test data of the high Yb/Hf ratio zircon, the internationally used high Yb/Hf ratio standard sample Temora 2 is used to monitor the test data of the high Yb/Hf ratio zircon. The Hf isotopic compositions of Plešovice, 91500, and GJ-1 have been reported by (Zhang and Hu 2020). The Lu-Hf isotopic compositions of zircons from the magmatic rocks, together with the results for the standards used, are presented in Table S2.

**12. In-situ Nd isotope analysis of apatite by LA-MC-ICP-MS**

In-situ Nd isotope analysis of apatite grains was performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) equipped with a Geolas HD excimer ArF laser ablation system (Coherent, Göttingen, Germany) at Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. In the laser ablation system, helium was used as the carrier gas within the ablation cell and was merged with argon (makeup gas) after the ablation cell. Small amounts of nitrogen were added to the argon makeup gas flow to improve the sensitivity of Nd isotopes (Xu et al. 2015). The spot diameter ranged from 32 to 90 μm dependent on Nd signal intensity. The pulse frequency was from 4 to 10 Hz, but the laser fluence was kept constant at ~8 J/cm$^2$. A new signal-smoothing device was used downstream from the sample cell to efficiently eliminate the short-term variation of the signal and remove mercury from the background and sample aerosol particles (Xu et al. 2015). The Neptune Plus was equipped with nine Faraday cups fitted with $10^{11}\Omega$ resistors. Isotopes $^{142}$Nd, $^{143}$Nd, $^{144}$Nd, $^{145}$Nd, $^{146}$Nd, $^{147}$Sm, $^{148}$Nd, and $^{149}$Sm were collected in Faraday cups using static mode. The mass discrimination factor for $^{143}$Nd/$^{144}$Nd was determined using $^{146}$Nd/$^{144}$Nd (0.7219) with the exponential law. The $^{149}$Sm signal was used to correct the remaining $^{144}$Sm interference on $^{144}$Nd, using the $^{144}$Sm/$^{149}$Sm ratio of 0.2301. The mass fractionation of $^{147}$Sm/$^{149}$Sm was corrected by the $^{147}$Sm/$^{149}$Sm normalization, using the $^{147}$Sm/$^{149}$Sm ratio of 1.08680 and exponential law. All data reduction for the MC-ICP-MS analysis of Nd isotope ratios was conducted using the "Iso-Compass" software (Zhang et al. 2020). Two natural apatite megacrysts, Durango and MAD, were used as the unknown samples to verify the accuracy of the calibration method for in-situ Nd isotope analysis of apatite. The chemical and Nd isotopic compositions of Durango and MAD have been reported by (Zhang et al. 2020). The in-situ Nd isotopic compositions of apatite grains from the ESZ magmatic rocks, along with the results for the standards used (Durango and MAD), are presented in Table S3.

**13. REFERENCES**

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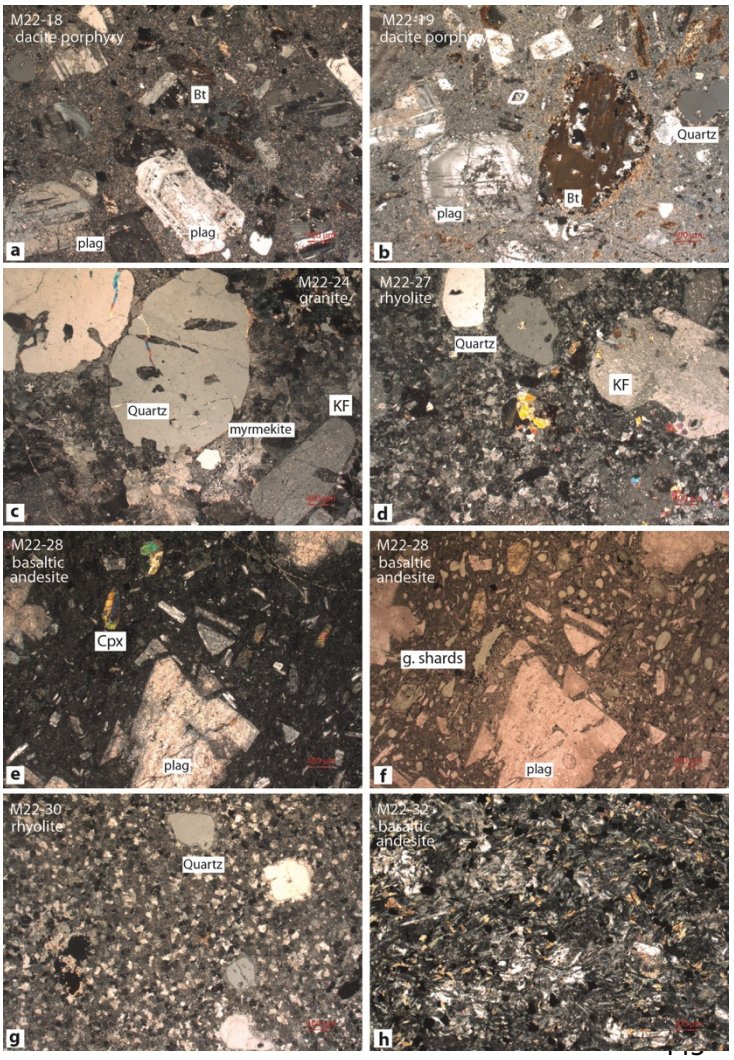


**Figure S1-** Microphotographs of magmatic rocks from the Güzel-Yayla prospect. (a-b) Porphyritic texture with large plagioclase and biotite phenocrysts and quartz microphenocrysts in a glassy to fine-grained groundmass. Plagioclase phenocrysts show zonation and sieve texture in the core. (c) Coarse-grained quartz and potassium feldspar crystals with myrmekitic intergrowths in Late Cretaceous granites. (d) Quartz microphenocrysts and altered potassium feldspar phenocrysts, alongside pleochroic epidote crystals, in a fine-grained felsic groundmass. (e) XPL and (f) PPL images of basaltic andesites with altered plagioclase porphyries, clinopyroxene laths in a fine-grained groundmass, and altered volcanic glass shards. (g) Quartz microphenocrysts in the altered cryptocrystalline groundmass of Tirebolu rhyolites. (h) Fine-grained plagioclase in a pilotaxitic texture in basaltic andesites.

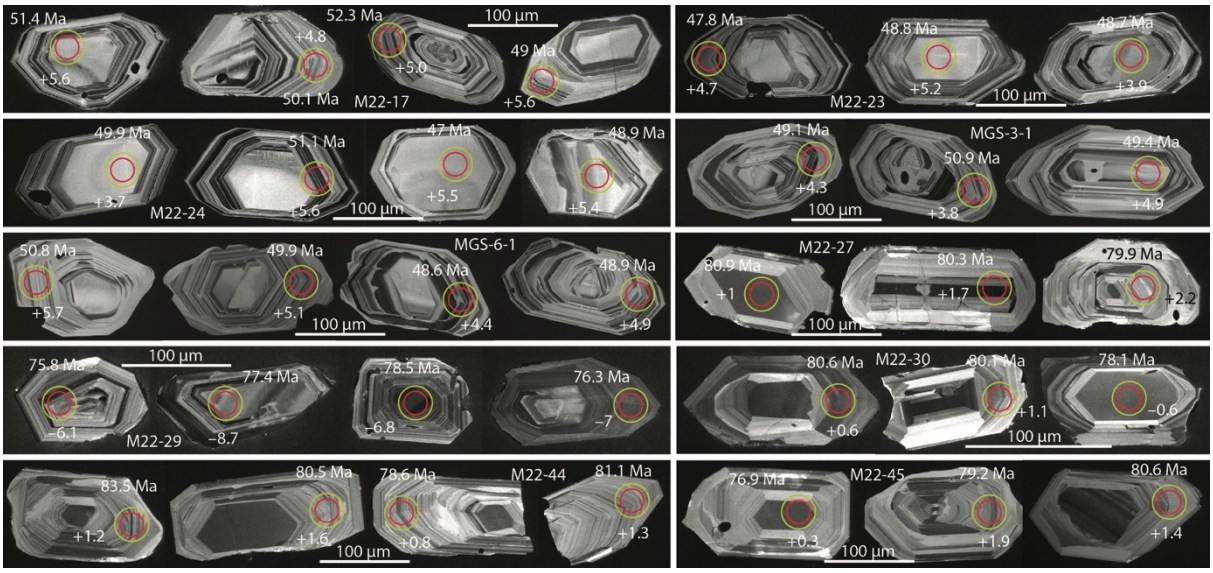


**Figure S2-** Cathodoluminescence images of zircons analyzed in this study for U-Pb dating from Güzel-Yayla Late Cretaceous and Eocene magmatic rocks. Red circles show U-Pb ages and yellow circles indicate εHf(t) values for zircon grains.

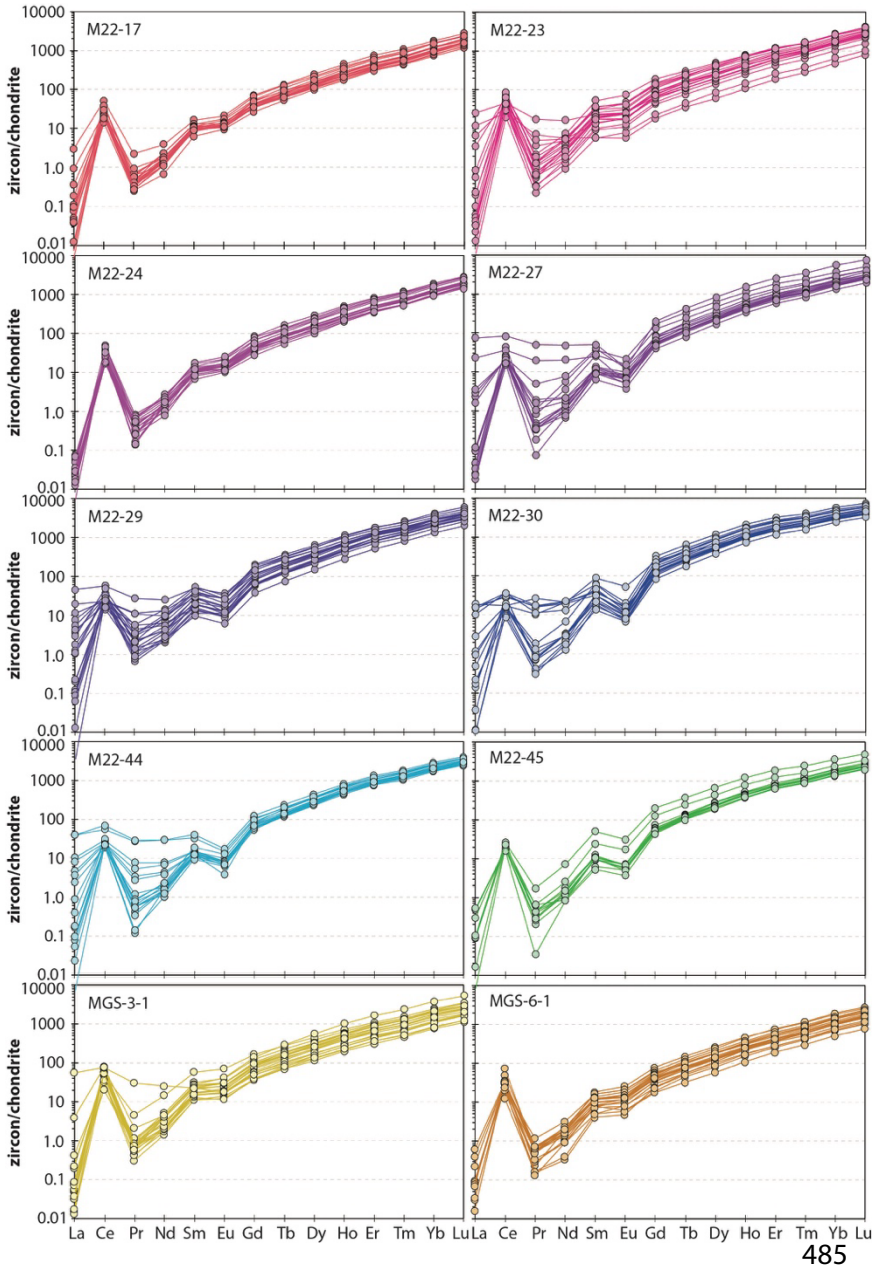


**Figure S3-** Rare-earth element compositions of zircons from Güzel-Yayla Late Cretaceous and Eocene magmatic rocks.

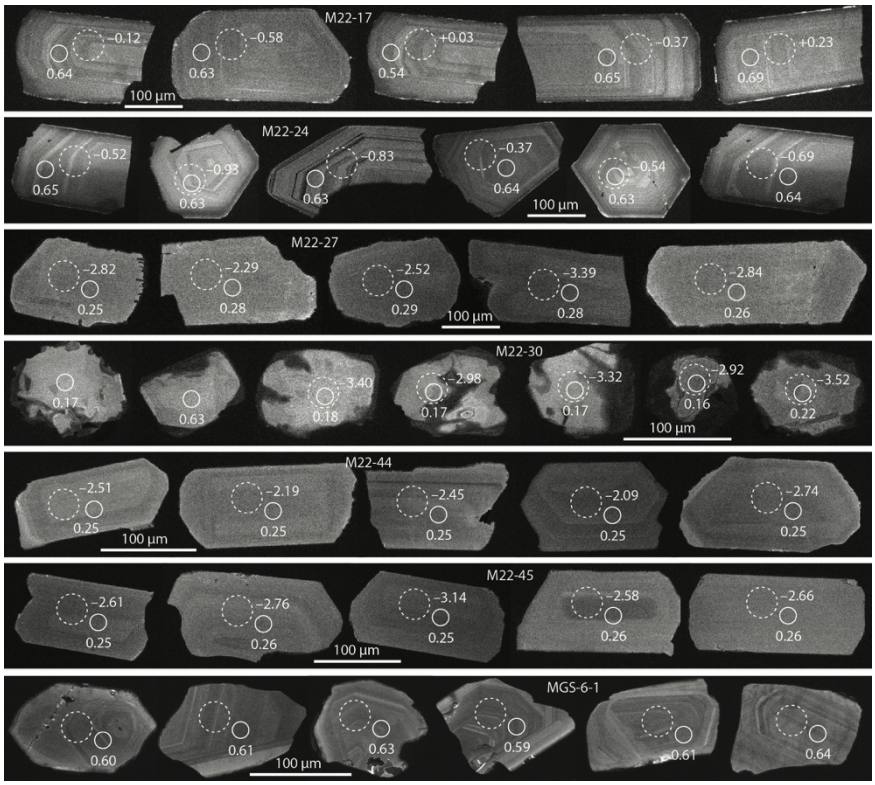


**Figure S4-** Cathodoluminescence images of apatite grains analyzed for major-trace elements and in-situ Nd isotope compositions from Güzel-Yayla Late Cretaceous and Eocene magmatic rocks. Small, dashed circles represent Eu/Eu* ratios, while large, dashed circles indicate εNd(t) values for apatite grains.

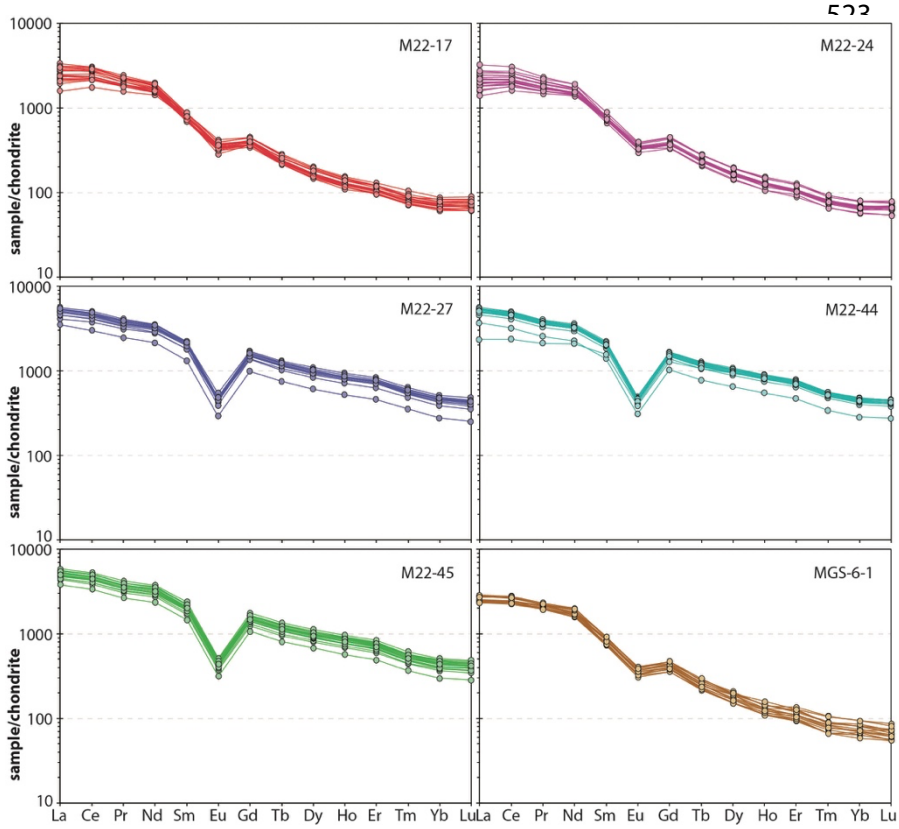


**Figure S5-** Trace element compositions of apatite, analyzed via LA-ICPMS, from Güzel-Yayla Late Cretaceous and Eocene magmatic rocks.