

Reconstructing crustal thickness evolution from europium anomalies in detrital zircons

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ABSTRACT

A new data compilation shows that in intermediate to felsic rocks, zircon Eu/Eu* [chondrite normalized $\text{Eu}/\sqrt{(\text{Sm} \times \text{Gd})}$] correlates with whole rock La/Yb, which has been used to infer crustal thickness. The resultant positive correlation between zircon Eu/Eu* and crustal thickness can be explained by two processes favored during high-pressure differentiation: (1) suppression of plagioclase and (2) endogenic oxidation of Eu^{2+} due to garnet fractionation. Here we calibrate a crustal thickness proxy based on Eu anomalies in zircons. The Eu/Eu*-in-zircon proxy makes it possible to reconstruct crustal thickness evolution in magmatic arcs and orogens using detrital zircons. To evaluate this new proxy, we analyzed detrital zircons separated from modern river sands in the Gangdese belt, southern Tibet. Our results reveal two episodes of crustal thickening (to 60–70 km) since the Cretaceous. The first thickening event occurred at 90–70 Ma, and the second at 50–30 Ma following Eurasia-India collision. These findings are temporally consistent with contractional deformation of sedimentary strata in southern Tibet.

INTRODUCTION

Crustal thickness profoundly influences a number of geologic processes including magmatic differentiation (Ducea, 2002; Ducea et al., 2015; Farner and Lee, 2017; Tang et al., 2018), ore formation (Kay, 2001; Lee and Tang, 2020), and erosion and weathering (Larsen et al., 2014). However, resolving the evolution of crustal thickness has been challenging. Because of erosion, weathering, and tectonic processes, the continental crust has been subject to constant destruction and overprinting after its formation, so the preserved continental crust may not reflect how thick it was when the crust was first generated.

Recent studies found that certain element ratios (e.g., Sr/Y and La/Yb) in intermediate to felsic rocks correlate with crustal thickness (Chapman et al., 2015; Profeta et al., 2015).

As the crust thickens, the increased pressure of magmatic differentiation enhances amphibole and/or garnet fractionation relative to plagioclase. Amphibole and garnet fractionations deplete middle and heavy rare earth elements (REEs), respectively, relative to light REEs and Sr. The La/Yb and Sr/Y approaches extract differentiation pressure and thus crustal thickness from magmatic records, and their effectiveness has been demonstrated by a number of studies of Phanerozoic orogens (Chapman et al., 2015; Farner and Lee, 2017; Haschke et al., 2002). Despite their successful applications, these whole rock chemistry methods require extensive sampling over large areas in the field, and sample availability can be strongly biased by accessibility; for deep time, their applications are further limited by the increasingly significant issue of preservation of rock records.

Here we extend the arena of rock chemistry-based crustal thickness proxies by linking zircon Eu anomaly to whole rock La/Yb ratio.

Zircon is ubiquitous in the continental crust and can survive most metamorphic, erosional, and weathering processes due to its refractory nature. Detrital zircons naturally sample large areas exposed to erosion and may fill gaps in Earth's history where rock records are missing (Balica et al., 2019; McKenzie et al., 2016, 2018; Zhu et al., 2020). We first calibrate the zircon crustal thickness proxy against the whole rock La/Yb proxy. Then, we evaluate the zircon proxy with a case study of the Gangdese belt, southern Tibet, where independent geologic constraints on crustal thickening and/or shortening exist.

RATIONALE

Europium anomaly [Eu/Eu*; chondrite normalized $\text{Eu}/\sqrt{(\text{Sm} \times \text{Gd})}$] in zircon is dictated by Eu/Eu* in the melt and Sm-Eu-Gd partitioning between zircon and melt. Unlike other REEs which are trivalent (except Ce), Eu exists as both Eu^{2+} and Eu^{3+} in most magmatic systems. Eu^{2+} is geochemically similar to Sr^{2+} and thus strongly partitions into plagioclase (Ren, 2004). Plagioclase fractionation causes Eu depletion relative to neighboring Sm and Gd in the residual melt. As a consequence, zircons crystallizing from the residual melt would have negative Eu anomalies, or $\text{Eu}/\text{Eu}^* < 1$ (Holder et al., 2020). Eu/Eu* in zircon is also sensitive to $\text{Eu}^{2+}/\text{Eu}^{3+}$ in the melt because Eu^{2+} is significantly more incompatible than Eu^{3+} in zircon lattice, as inferred from Sr^{2+} partitioning in zircon (Thomas et al., 2002).

As the crust thickens, the intracrustal differentiation through anatexis or fractional crystallization takes place at higher pressures, which suppresses plagioclase (e.g., Green, 1982) and

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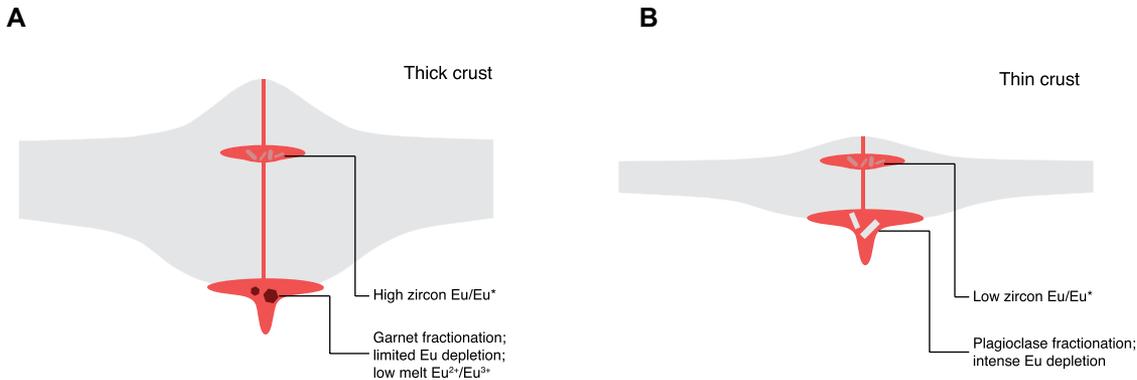


Figure 1. Cartoon (not to scale) showing influence of crustal thickness on Eu systematics in intracrustal differentiation. Crustal thickening destabilizes plagioclase and stabilizes garnet in deep crust, which reduces Eu depletion and oxidizes Eu in derivative melt. Eu/Eu^* —chondrite normalized $\text{Eu}/\text{Eu}^* = \text{chondrite normalized } \text{Eu}/\sqrt{(\text{Sm} \times \text{Gd})}$.

thus prevents Eu depletion in the melt. In addition, intense crustal thickening stabilizes garnet, which preferentially sequesters Fe^{2+} over Fe^{3+} from the melt. The elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ (ferric Fe to total Fe ratio) in the melt would then oxidize multivalent trace elements such as Eu (Tang et al., 2018, 2019). Europium oxidation converts the less-compatible Eu^{2+} to more-compatible Eu^{3+} , which enhances Eu partitioning in zircon. The collective effect is that zircon Eu/Eu^* increases with increasing crustal thickness (Fig. 1).

CALIBRATING THE Eu/Eu^* -IN-ZIRCON CRUSTAL THICKNESS PROXY

We compiled 120 igneous samples with paired zircon–whole rock composition data. These samples are from 29 localities around the world. The whole rocks generally have interme-

diate to felsic compositions with SiO_2 contents of 55–75 wt%. We did not include more mafic samples because mafic rocks are not important sources of zircon; we also ignored high-silica samples ($\text{SiO}_2 > 75$ wt%) because Eu systematics may be complicated by extreme differentiation (Fig. S3 in the Supplemental Material¹). We divided our compiled samples into post-Archean and Archean groups. Post-Archean samples were further divided into I-type (igneous protoliths), S-type (sedimentary protoliths), A-type (shallow emplacement) granitoids based on the classification in the source literature. The Archean samples are represented by TTGs

(tonalite-trondhjemite-granodiorite), which belong to I-type by definition.

I-type, including Archean TTGs, and A-type samples all fall on a positive correlation between zircon Eu/Eu^* and whole rock $[\text{La}/\text{Yb}]_N$ (the subscript N denotes chondrite normalized) (Fig. 2A). This prominent relationship suggests that, on the first order, Eu/Eu^* in zircon is controlled by the differentiation pressure which correlates with crustal thickness (McKenzie et al., 2018), despite the various complexities associated with global sample compilation. In particular, redox conditions seem to play a less-important role in determining Eu/Eu^* in zircons from felsic magmas, or redox conditions of felsic magmas also correlate with differentiation pressure in most I- and A-type granitoids (Tang et al., 2018, 2019). S-type samples show no correlation between zircon Eu/Eu^* and whole

¹Supplemental Material. Methods, supplemental figures, and data. Please visit <https://doi.org/10.1130/GEOL.S.12869660> to access the supplemental material, and contact editing@geosociety.org with any questions.

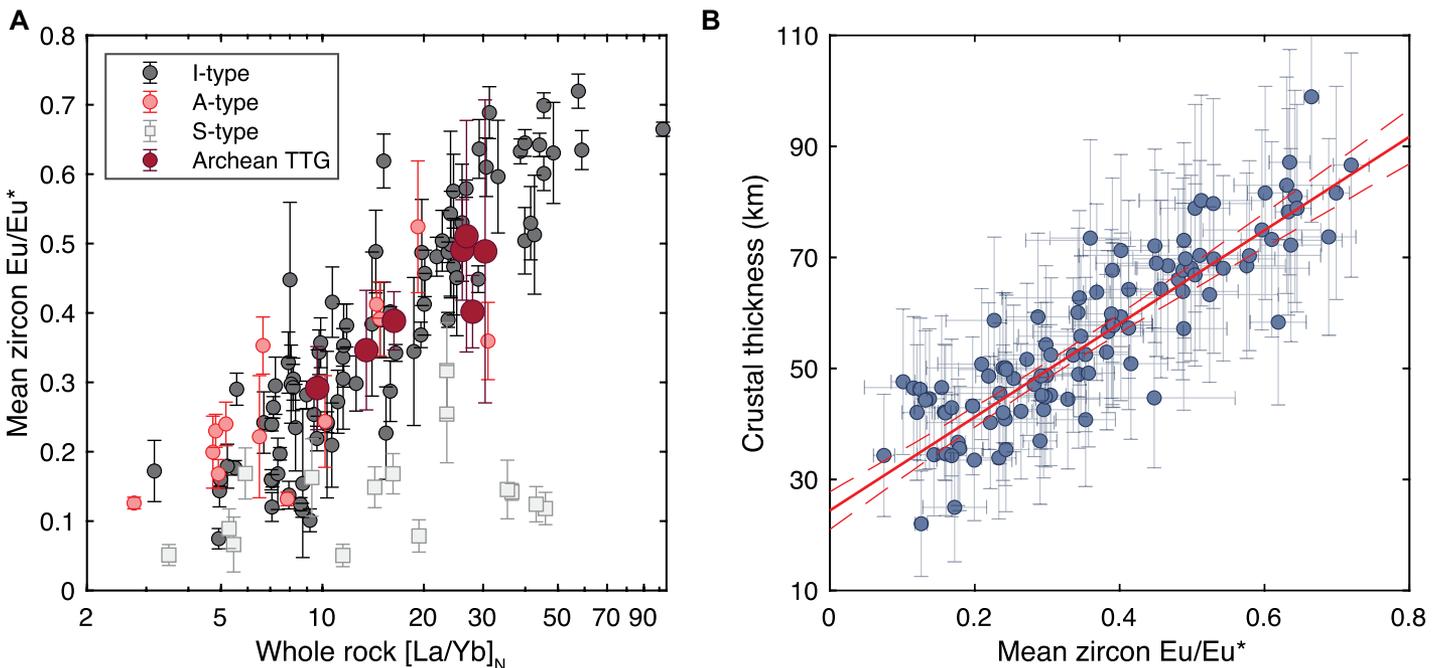


Figure 2. (A) Zircon Eu/Eu^* [chondrite normalized $\text{Eu}/\sqrt{(\text{Sm} \times \text{Gd})}$] versus whole rock $[\text{La}/\text{Yb}]_N$ (N—chondrite normalized). (B) Crustal thickness–zircon Eu/Eu^* regression. Each data point represents mean of multiple analyses of zircons extracted from individual rock sample. Errors are two standard errors. Linear regression (mean and 95% confidence interval shown by the solid and dashed red lines, respectively) in B was obtained using post-Archean I-type samples, post-Archean A-type samples, and Archean tonalite-trondhjemite-granodiorite (TTG) samples. Errors of crustal thickness were derived from Profeta et al. (2015).

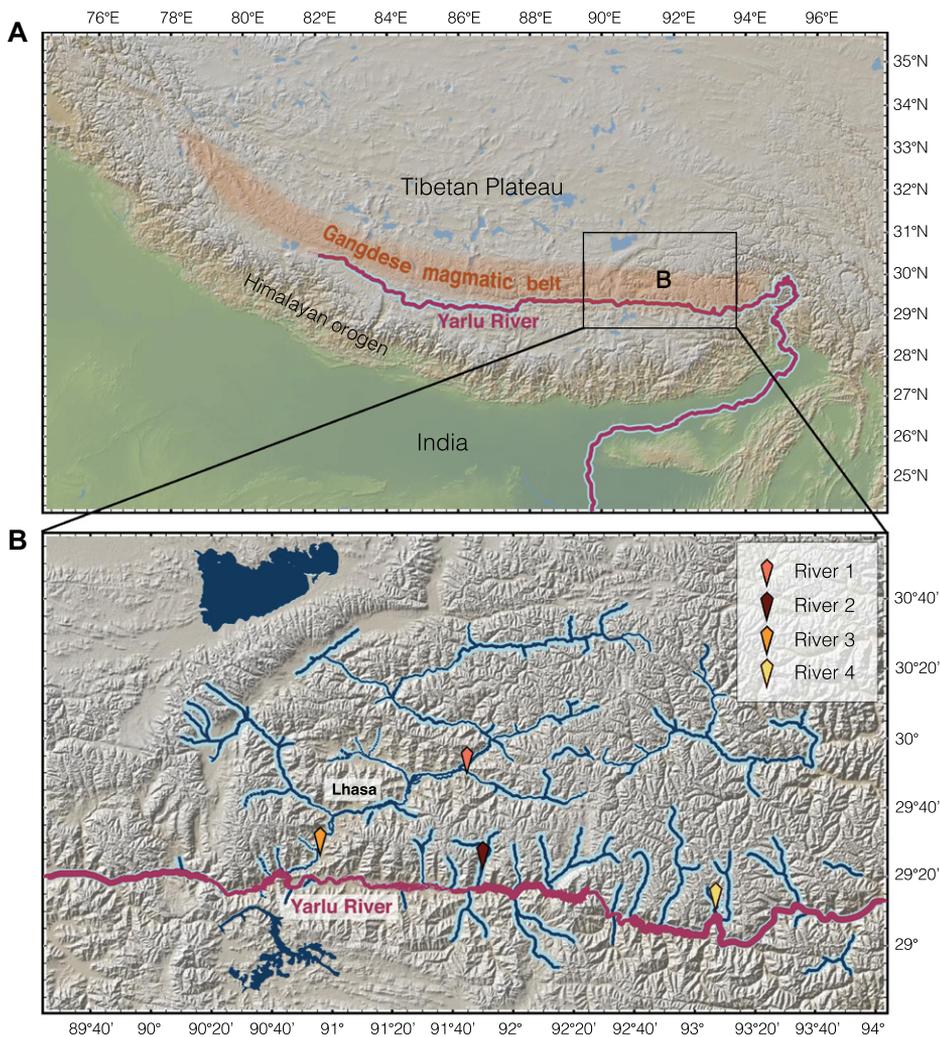


Figure 3. Maps showing river sand collecting sites and tributaries of the Yarlu River (Yarlung Tsangpo) in the sampling area, southern Tibet. All sand samples were collected in tributaries instead of the Yarlu River, which also receives detritus from the Himalayan orogen to the south. GeoMapApp software (<http://www.geomapapp.org/>) was used in making maps.

rock $[La/Yb]_N$ (Fig. 2A). The consistently low Eu/Eu^* in these samples is likely inherent from the sedimentary protoliths derived from the Eu-depleted upper continental crust (Rudnick and Gao, 2014). Alternatively, the sedimentary protoliths of S-type granitoids may contain substantial amounts of reduced phases such as graphite and sulfides (Burnham and Berry, 2017; Chappell and White, 1992) that lead to highly reduced conditions and conversion of Eu^{3+} in the melt to less-compatible Eu^{2+} .

The positive correlation between zircon Eu/Eu^* and whole rock $[La/Yb]_N$ in most intermediate to felsic samples affirms the feasibility of using zircon Eu/Eu^* to reconstruct crustal thickness (McKenzie et al., 2018). Using modern arc samples, Profeta et al. (2015) derived an empirical relationship between whole rock $[La/Yb]_N$ and crustal thickness. Combining this relationship with the correlation between zircon Eu/Eu^* and whole rock $[La/Yb]_N$ (Fig. 2B), we arrived at

an empirical equation that calculates crustal thickness from zircon Eu/Eu^* (Fig. 2B):

$$z = (84.2 \pm 9.2) \times Eu/Eu^*_{zircon} + (24.5 \pm 3.3), \quad (1)$$

where z is crustal thickness (in km). The uncertainties of the slope and intercept are two standard deviations. In this linear regression, we used all of our compiled samples except the S-type samples because their zircon Eu/Eu^* does not correlate with whole rock $[La/Yb]_N$.

APPLICATION OF THE Eu/Eu^* -IN-ZIRCON CRUSTAL THICKNESS PROXY IN SOUTHERN TIBET

Our new proxy makes it possible to reconstruct crustal thickness using detrital zircons. The Gangdese magmatic belt in southern Tibet provides an ideal case to evaluate this proxy. Southern Tibet transitioned from an Andean-type convergent margin in the Mesozoic to a collisional orogen in the Cenozoic (Allégre

et al., 1984). The Gangdese belt has been magmatically active in the last ~200 m.y. (Chu et al., 2006), and the batholith is dominated by I-type granitic rocks at all ages (Ji et al., 2009).

We collected river sands from four modern rivers draining the eastern Gangdese batholith (Fig. 3). Detrital zircons were separated from these river sands and analyzed for simultaneous U-Pb ages and trace elements by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). We measured a total of 1639 detrital zircons. Detailed descriptions of the analytical methods and data are provided in the Supplemental Material. We removed analyses with $Th/U < 0.1$ and/or $La > 1$ ppm to eliminate metamorphic zircons and the data compromised by inclusions (Hoskin and Schaltegger, 2003). When calculating age-binned average crustal thickness, we removed analyses showing the highest 10% and lowest 10% Eu/Eu^* within each 5 m.y. interval to reduce scatter. This screening procedure does not change the calculated crustal thickness pattern (Fig. S5).

Our reconstructed crustal thickness shows that the Gangdese belt started with a crustal thickness of ~40 km in the Early Cretaceous, then gradually thickened to ~60 km at ca. 80 Ma. The crust then thinned to ~50 km before it thickened again to ~70 km starting in the Eocene (Fig. 4A). Overall, the crustal thickness pattern reconstructed from detrital zircons mirrors that calculated using whole rock La/Yb , although some inconsistencies exist where the sample densities are low for both zircons and rocks (Fig. 4).

Opinions diverge when it comes to the crustal thickness in the Late Cretaceous. Both whole rock geochemistry and detrital zircon Eu/Eu^* point to high-pressure origins for the Late Cretaceous granites in the Gangdese batholith. Ji et al. (2014) attributed the high La/Yb and Sr/Y ratios in the Late Cretaceous granites to intense crustal thickening, whereas Zhu et al. (2017) suggested these granites might have been generated by slab melting without crustal thickening. Zircon Eu/Eu^* cannot distinguish between high-pressure intracrustal differentiation and slab melting, but the Late Cretaceous thickening scenario is more consistent with a number of regional geologic observations including sedimentary strata transitioning from marine limestone to clastic red beds followed by contractional deformation, north-south crustal shortening in the Lhasa terrane, and progressive burial of middle to lower crustal rocks in the Gangdese belt at that time (Burg et al., 1983; Kapp et al., 2007; Leier et al., 2007; Cao et al., 2020).

It is interesting to note that the crustal thickness decreased by ~10 km at the end of the Cretaceous (Fig. 4A). One possible explanation is that the lower crust was delaminated (Ji et al., 2014). Coupled magmatism and

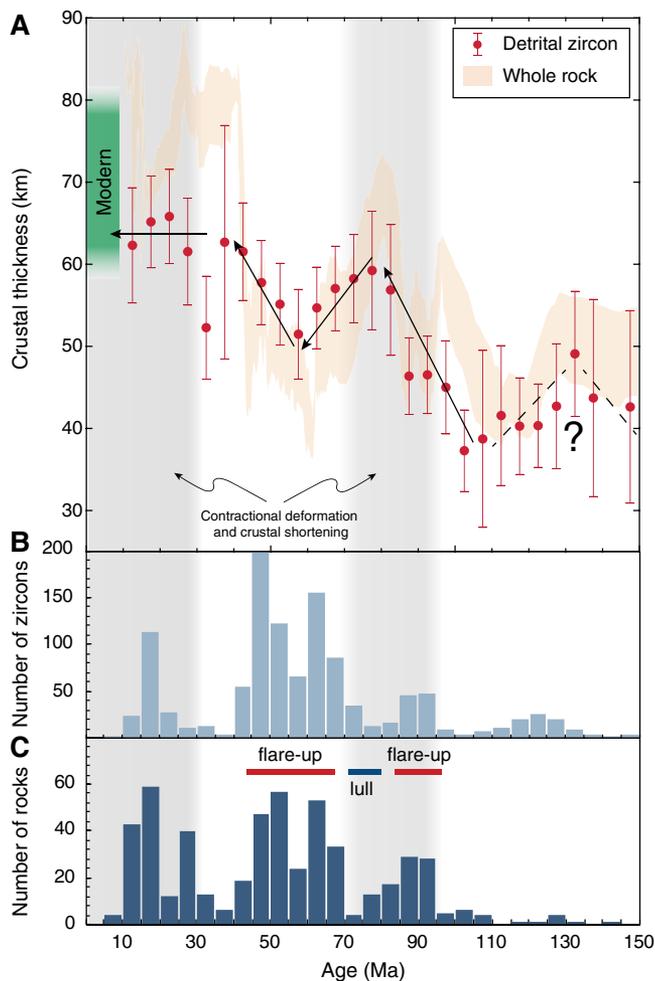


Figure 4. (A) Crustal thickness evolution of the Gangdese magmatic belt, southern Tibet, reconstructed from Eu/Eu^* [chondrite normalized $\text{Eu}/\sqrt{(\text{Sm} \times \text{Gd})}$] in detrital zircons ($n = 1477$). Data are plotted as binned averages for every 5 m.y. interval with two standard errors. Also shown here is crustal thickness calculated using the whole-rock La/Yb method (Profeta et al., 2015), plotted as running averages with two-standard-error intervals (orange band). Gangdese whole-rock La/Yb data are from Chapman and Kapp (2017). Timing of contractional deformation and crustal shortening in southern Tibet is from Kapp et al. (2007) and Leier et al. (2007). Black arrows and dashed lines illustrate the arbitrary trends of crustal thickening and thinning. (B) Age distribution of detrital zircons analyzed in this study. (C) Age distribution of Gangdese magmatic rocks compiled by Ji et al. (2014).

crustal shortening may have produced a thick layer of garnet-bearing cumulates (arclogites) in the lower Gangdese arc crust at ca. 70 Ma. These deep-arc cumulates are denser than the underlying peridotites and may eventually sink into the mantle. Alternatively, the Gangdese belt may have undergone a ~20 m.y. transient extension in response to slab rollback (Wang et al., 2015; Zhu et al., 2015). This transient extension may have triggered the magmatic flare-up at the Mesozoic-Cenozoic boundary (Fig. 4).

CAVEATS AND LIMITATIONS

Although the average zircon Eu/Eu^* systematically increases with increasing whole rock La/Yb (Fig. 2A), significant scatter exists within individual samples (Fig. S2). A variety of factors may contribute to this scatter. For example, plagioclase co-crystallizing with zircon in the shallow magma chambers may deplete Eu in the melt and cause low Eu/Eu^* in zircon. Assimilation of matured crustal materials may also affect Eu/Eu^* in the melt and thus Eu/Eu^* in zircon. Redox variation in melts changes Eu valence state and thus Eu partitioning in zircon (Holder et al., 2020). Given these complexities, the robustness of the calculated crustal thick-

ness can be sensitive to the number of zircon analyses. We suggest that a histogram of zircon age distribution (Fig. 4B) should be provided side by side with the calculated crustal thickness evolution. We further suggest that interpretations of crustal thickness changes should be made based on evolution patterns instead of isolated anomalies.

S-type granitoids may also complicate the use of detrital zircons to reconstruct crustal thickness because Eu/Eu^* in S-type granitoid zircons does not reflect crustal thickness (Fig. 2A). The Gangdese belt presents a simple case where S-type granitoids are scarce. But in other orogens, S-type granitoids may be a more important source of detrital zircons. Zircons from S-type granitoids can be identified by their phosphorus contents (Burnham and Berry, 2017; Zhu et al., 2020), and should be filtered out before applying the zircon crustal thickness proxy in places with complex lithologies.

Finally, our proxy may not apply to zircons crystallized from high-silica melts ($\text{SiO}_2 > 75 \text{ wt}\%$) due to complex Eu/Eu^* systematics and an overstretch of the whole rock La/Yb proxy in these extremely differentiated samples. However, we find that igneous rocks with SiO_2

$> 75 \text{ wt}\%$ are minor (~5% in magmatic arcs; Fig. S3) and are probably dominated by S-type granitoids whose zircons can be filtered out by their phosphorus contents.

CONCLUSIONS AND OUTLOOK

Zircon Eu/Eu^* positively correlates with whole rock $[\text{La}/\text{Yb}]_N$ in most intermediate to felsic igneous samples. This correlation allows one to use zircon Eu/Eu^* to estimate the La/Yb of the parent magmas, which in turn gives crustal thickness. Application of the Eu/Eu^* -in-zircon crustal thickness proxy to Gangdese detrital zircons reveals at least two episodes of crustal thickening in the last 150 m.y. that are in phase with field observations in the Gangdese magmatic belt.

Our Eu/Eu^* -in-zircon crustal thickness proxy is not to replace whole rock trace element proxies, but the zircon approach opens the window for extracting crustal thickness information from the extensive detrital zircon archive and may provide a continuous record of crustal thickness evolution. By integrating age, geochemistry, and crustal thickness, the detrital zircon archive can now be used to reconstruct coupled tectonic and magmatic history in continental evolution.

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