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Detrital rutile tracks the first appearance of subduction zone low T/P paired metamorphism in the Palaeoproterozoic

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ABSTRACT

Earth is unique in the Solar System as the only planet characterised by an active plate tectonic regime. However, there is still no consensus on whether this was fully operational in the Archaean or if it did not develop until the Proterozoic. The metamorphic record offers valuable insight into this debate, since paired, high and low T/P metamorphic conditions are a hallmark of modern plate tectonics. However, much of the metamorphic rock record has either been eroded or overprinted by subsequent tectonothermal events. To address this issue, we examine the detrital rock record and evaluate the potential of rutile, a mineral that forms during subduction and deep-crustal metamorphic processes, as a proxy to track the existence of low T/P and paired metamorphism. At temperatures of 550 °C, rutile is mostly stable at pressures higher than ca. 13 kbar. We use this relationship and the Zr-in-rutile thermometer to determine peak metamorphic temperatures of detrital rutile grains to track

the temporal distribution of low T/P metamorphism. We have compiled a dataset of detrital metamorphic rutile from Archaean to Permian age to trace the occurrence of low and high T/P metamorphism through time. The earliest evidence of low T/P from detrital rutile is at about 2.1 Ga. This agrees with the earliest evidence of eclogite facies conditions from the rock record and it also implies that these conditions must have been more prevalent than the present rock record seems to indicate. Together, our study confirms that subduction zone low T/P metamorphism has been fully operating since at least the late Palaeoproterozoic.

Keywords: metamorphic proxy; low T/P metamorphism; paired metamorphism; detrital rutile; plate tectonics; Palaeoproterozoic

1. INTRODUCTION

The cyclic formation of supercontinents by modern plate tectonics is of critical importance to the secular evolution of the Earth System. It impacts, for example, the oxygenation of the atmosphere (Campbell and Squire, 2010), nutrient addition to the oceans (Reinhard et al., 2017; Zerkle, 2018), and the geological record itself (Dhuime et al., 2017; Li et al., 2003). Earth experienced major changes between 3 and 2 Ga (Cawood et al., 2018; Condie, 2018; Brown et al., 2020), including variations in the composition of the continental crust (Laurent et al., 2014a), and a change in the rate of continental growth (Dhuime et al., 2012). Several of these changes have been linked to the onset of subduction as a response to the secular cooling of the mantle. However, subduction may have been localized and unstable on the early Earth and therefore may not in itself provide evidence for modern plate tectonics, which requires sustained subduction (Brown et al., 2020; Cawood et al., 2018). It is therefore necessary to investigate the geological record for evidence of the major hallmarks of modern plate tectonics, namely the existence of self-sustained, interlinked subduction systems (Lenardic, 2018).

The metamorphic rock record provides strong evidence for sustained subduction for at least the last 700 million years (Brown et al., 2020; Brown and Johnson, 2018; Stern,

2005) with the prevalence of low-temperature eclogite and blueschist facies, and paired metamorphism. This record of cold-subduction is widespread in the Phanerozoic (Brown and Johnson, 2018), but the apparent absence of evidence for low geothermal gradients (T/P) in the greater part of the Proterozoic and during the Archaean (Brown et al., 2020; Brown and Johnson, 2018) has been argued as indicating that a different tectonic regime prevailed prior to the Neoproterozoic (Kusky, 2020; Stern, 2005). Exceptionally, late Palaeoproterozoic, partially retrogressed eclogite units have been reported (e.g. François et al., 2018; Ganne et al., 2012; Melnik et al., 2021; Weller and St-Onge, 2017), providing a growing body of evidence for cold-subduction and strong plates that allowed the exhumation of these units. However, due to the rather fragmentary and scarce repository of rocks recording these conditions, the assertion that modern plate tectonics has been fully operating since then has proven contentious. The period between the Palaeoproterozoic and the early Neoproterozoic may be characterized by an intermediate plate tectonic cycle between early Earth and modern-like endmembers (Brown and Johnson, 2018).

The identification of certain metamorphic conditions relies on the preservation of indicator minerals; for example, the presence of lawsonite or glaucophane is indicative of HP conditions. However, these hydrous mineral phases are prone to dehydration reactions during retrogression from HP conditions (Skelton et al., 2019; Tsujimori et al., 2006) and therefore pristine blueschist and low- T eclogite are rare even in the modern rock record (Lombardo and Rolfo, 2000; Whitney and Davis, 2006). In this study, we aim to provide a new way of probing the metamorphic record and assessing preservation bias, particularly of low T/P metamorphism, by using detrital rutile.

Rutile most commonly occurs after Ti-bearing precursors in intermediate to high pressure metamorphic rocks, particularly the latter (Angiboust and Harlov, 2017; Liou et al., 1998; Zack and Kooijman, 2017). It is also found within upper amphibolite and granulite facies terrains, and associated with either magmatic or lower temperature and pressure settings due to fluid precipitating processes (Carruzzo et al., 2006; Gonçalves et al., 2019;

Kotková and Harley, 2010). More rarely, rutile has been described as replacing ilmenite at intermediate grades (480-550 °C) in metapelites (Luvizotto et al., 2009). Alongside its higher stability at high pressures, Zr concentrations in rutile are temperature-dependent (Kohn, 2020; Tomkins et al., 2007; Zack et al., 2004a). Together, this makes rutile an ideal candidate to be used as a proxy of low T/P metamorphism. Although rutile can re-equilibrate during retrogression from higher metamorphic conditions, it is more robust than other minerals such as lawsonite and glaucophane that due to their hydrated nature are prone to re-equilibrate more readily. Rutile is also ubiquitous in detrital rocks, and thus it commonly survives weathering and transport. By investigating the sedimentary archive using detrital rutile we expect to be able to develop a more complete picture of the metamorphic record through time, compared with that derived from currently exposed metamorphic terrains (Brown and Johnson, 2019). This approach will allow: 1) tackling the individual metamorphic evolution of Precambrian terranes whose current crustal exposure is from deeper orogenic roots and thus bias the known metamorphic record towards higher-grade conditions, and 2) investigating Earth's long term metamorphic secular evolution, and its tectonic drivers, at a global scale.

2. SAMPLES, APPROACH AND METHODS

We have investigated published Zr-in-rutile geothermometry data from metamorphic rocks (appendix 1) to evaluate the potential of rutile as a proxy for low T/P metamorphism and some of the limitations associated with this approach. We also looked at detrital rutile datasets reporting U-Pb ages and a complete range of trace element data that are required for source discrimination and geothermometry, that include Cr, Zr, Nb, Sn, Hf, Ta and W. This results in the first combined data compilation of detrital rutile, using data from six published datasets (Agangi et al., 2020; Flowerdew et al., 2019; Rösel et al., 2018, 2014; Şengün et al., 2020; Zhou et al., 2020), from different regions and depositional ages, culminating in a dataset of detrital rutile ages ranging from the Permian to the Archean (appendix 2). To complement this dataset, we collected new trace element data from 161 U-

Pb concordant detrital rutile grains, from samples collected in NW Scotland. These correspond to a stratigraphic succession of Neoproterozoic to Cambrian in age: the Torridon Group and the Ardvreck Group, Eriboll Formation. Six samples were prepared from these units (3 from the Torridon Grp. and 3 from the Eriboll Fm.) and rutile grains were handpicked after common mineral separation procedures (see Pereira et al., 2019). Sample locations and U-Pb data for these rutile grains are presented and discussed in Pereira et al. (2020). U-Pb concordant rutile grains were then subjected to trace element analysis using LA-ICPMS. BSE images were used to target the same domains as sampled during the U-Pb isotopic analysis. Rutile grains included in this study are mostly homogeneous, with no apparent BSE (trace element composition) zonation, and yield U-Pb ages ranging from 1.0 to 2.9 Ga. The total dataset comprises 840 analyses (appendix 4).

Trace element microanalysis by Laser ablation coupled inductively plasma Mass Spectrometry (LA-ICPMS)

Trace elements in rutile were determined using an ASI RESOLUTION 193nm ArF excimer laser coupled to the ANALYTIK JENA Plasma Quant Elite quadrupole ICP-MS at the University of Portsmouth (UoP). Rutiles were ablated with laser beam diameters between 25 and 40 μm , using an energy density of $\approx 4.0 \text{ J/cm}^2$ and a repetition rate of 5 Hz. Analyses consisted of 20 s background, 30 s ablation and sample acquisition, and 5 s of washout, resulting in 55 s per analysis. Instrumental parameters and ablation conditions are summarized in the supplementary file A. The following isotopes were analysed: ^{49}Ti , ^{29}Si , ^{25}Mg , ^{45}Sc , ^{51}V , ^{52}Cr , ^{87}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{95}Mo , ^{118}Sn , ^{121}Sb , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{177}Hf , ^{181}Ta , ^{182}W , ^{208}Pb , ^{232}Th and ^{238}U .

A sample-standard bracketing method was used to correct for instrumental drift using BCR-2 as the reference material (using reported concentrations from Jochum et al. (2005)). R10 (GEOREM database), BHVO (using reported concentrations from Jochum et al. (2005)) and NIST610 and 612 (reported concentrations from Jochum et al. (2011)) were used as

secondary standards, analysed between unknowns and primary standards in the sample-standard bracketing method. NIST610 and R10 were analysed using a 40 μm laser beam diameter. In contrast, for the BHVO reference material, a laser beam of 80 μm diameter was used to directly access the attenuation mode of the ANALYTIK JENA ICP-MS, important for stable measurement of ^{49}Ti . TiO_2 was used as an internal standard to normalise the intensity of all unknowns, using reference reported values for glasses, and using Ti of 58.8 wt% for all rutile grains). Data were processed using the software package IOLITE 3.31. For Zr, we obtained 5% accuracy relative to published values for all glass standards, within 5% from published values for R10 (GEOREM database) and a 0.06 ppm detection limit. The full instrumental and analytical setup and standard data can be found in appendix 3.

3. ZR-IN-RUTILE GEOTHERMOMETRY APPLIED TO DETRITAL GRAINS

3.1 Application of the Zr-in-rutile thermometer

The Zr-in-rutile thermometer has been calibrated based on natural samples by Zack et al. (2004). Several other researchers have subsequently refined the calibration, including Tomkins et al. (2007) who demonstrated a minor pressure dependency, more significant in the alpha-quartz field. These calibrations have been recently revisited by Kohn (2020) who used new natural data, refined previous natural datasets, and combined them with published experimental data into a new equation that we use in this study. In Figure 1, a comparison between temperature estimates obtained by Zr-in-rutile and mineral equilibria using conventional thermobarometry from 14 published studies (appendix 1) is presented. In most circumstances, thermobarometry based on element exchange between mineral pairs yields a larger uncertainty than single grain thermometers (Fig. 1). Uncertainties in applying this calibration are around 10-15 $^{\circ}\text{C}$, which is often the variation achieved taking into account the uncertainty in the assumed pressure (Fig. 1). On the other side, the standard deviation of Zr concentrations between grains within the same sample propagates into a larger uncertainty that often exceeds that obtained from mineral equilibria (Fig. 1).

The linear correlation between both methods is consistent, yielding a ratio not far from 1 (Fig. 1A). This correlation is improved if the temperature estimate used for the correlation taken from mineral equilibria is adjusted to its uncertainty ($R^2 = 0.72$; Fig 1B). For instance, often peak conditions are given as a range, and the true value is enclosed in the interval. Instead of the average, we compare the T estimate determined from Zr-in-rutile and check whether the temperature is enclosed by the interval. If so, the value is taken as the true average T for the correlation. Where this difference is larger than the interval, the uncertainty from the average T estimate from mineral equilibria is either summed or subtracted to obtain the best correlation scenario. In doing so, it becomes clear that for most samples, average Zr concentrations and their uncertainties have a robust fit with the thermobarometric estimate of their rocks, with a tendency line that is essentially 1:1 (Fig.1).

Regardless of the calibration equation, rutile has to be in equilibrium with zircon and quartz, so that $t\text{-ZrO}_2$ and $\alpha\text{-quartz}$ activities are 1. As Triebold et al. (2012, 2007) demonstrate, by applying a discrimination diagram based on Cr and Nb (Meinhold et al., 2008; Zack et al., 2004b), rutile grains that have metafelsic affinity can be presumed to have formed in such conditions. Therefore, a filter was applied to enable distinction between probable protolith sources, and thus to infer silica activity in the system. By applying the $\log(\text{Cr/Nb})$ following Meinhold et al. (2008), grains with $\log(\text{Cr/Nb}) < 0$ and Nb > 800 ppm were considered as metafelsic and thus yield $a_{\alpha\text{-quartz}} = 1$, whereas grains with $\log(\text{Cr/Nb}) > 0$ or Nb < 800 ppm were considered metamafic and the $\alpha\text{-quartz}$ activity is unknown. While at amphibolite facies conditions this discrimination can sometimes fail (metamafic being classified as metafelsic), we stress that metamafic rocks can have $a_{\alpha\text{-quartz}} = 1$. Felsic rocks commonly yield zircon and therefore we assume that grains classified as metafelsic-derived yield $a_{t\text{-ZrO}_2} = 1$. Therefore, by applying this filter, we have a high level of confidence in the Zr-in-rutile thermometry outputs. The statistically comprehensive dataset compiled from the literature (supplementary file B) shows that only about 10 % of the cases (n total = 764) are false positives (i.e. a metamafic-derived grain being discriminated as metafelsic), and rarely

a felsic protolith is discriminated as mafic. It is important to note that from the dataset used to estimate this uncertainty, regardless of protolith composition, quartz was always present ($a_{\alpha\text{-quartz}} = 1$).

3.2 Zr concentration scatter and its significance

Zr-in-rutile has become a popular tool to retrieve peak temperatures from metamorphic rocks. Several issues have been systematically found from applying this thermometer (Cruz-Uribe et al., 2018; Kooijman et al., 2012; Pape et al., 2016), such as high Zr concentration deviations in grains from the high temperature domain ($> 800\text{ }^{\circ}\text{C}$; Fig. 2). Natural scatter present in most metamorphic rocks, and from the subset we have used (appendix 1), is not commonly observed in eclogite (Fig. 2) or blueschist-facies rocks (Gao et al., 2014; Hart et al., 2016), and when present, it is usually envisaged as recording multiple stages during prograde growth (Spear et al., 2006). This imparts some uncertainty when applying this tool to detrital rutile, as one single estimate can represent either the prograde history or natural scatter by other competing processes (e.g., diffusion, local equilibrium, recrystallisation).

While scattering of Zr concentration in rutile is commonly present in rocks at higher metamorphic grade, the scatter is significantly more limited at a lower grade, regardless of protolith composition (Fig. 2). The significant data scatter in high grade rocks (granulite, migmatite) amounts to commonly less than or around $100\text{ }^{\circ}\text{C}$ (including rutile as inclusions in other minerals and matrices), but at lower temperatures it implies an overall standard deviation of $\pm 50\text{-}60\text{ }^{\circ}\text{C}$ or even less. Importantly, minimum values/outliers of the higher-grade rutile grains are never lower than $600\text{ }^{\circ}\text{C}$ (Fig. 2), suggesting that re-equilibration does not seem to take place below those temperatures.

3.3 Temperature estimates, uncertainties, and assumptions

In the approach taken here, we have no independent pressure proxies that can assist in further distinguishing metamorphic grade/geothermal gradient (e.g., blueschist vs low-T

eclogite, amphibolite vs eclogite, high-T eclogite vs granulite). However, a few important assumptions (e.g., constraints on rutile phase stability, Zr diffusion behaviour), support the identification of rutile grains equilibrated at low T/P (Fig. 3). Because at lower temperatures, rutile is not commonly stable at lower than 10 to 12 kbar (Fig. 3; for all types of rock compositions), this implies that all rutile yielding temperatures lower than 550 °C (intersection of minimum low T/P with the rutile-out boundary; yellow star in Fig. 3) will be a proxy for blueschist facies conditions (and low T/P in general).

One of the challenges of utilising Zr concentrations to retrieve peak-T also resides in the thermal histories of the source terranes. Because trace element contents can reset under certain conditions, the potential impact of Zr diffusion during cooling or overprinting during a more recent high temperature event (brown dashed lines, Fig. 3) has been considered in agreement with similar reviews from the literature (e.g., Kohn 2020; Tomkins et al., 2007). For a wide range of cooling rates (0.6 to 75 °C/Ma), rutile (ca. 200 µm) grains can start to re-equilibrate at mid- to upper-amphibolite facies during retrogression (Fig. 3). If the source terranes endured polymetamorphism, it would require about 50 Ma at mid-amphibolite/eclogite facies conditions to re-equilibrate the Zr in rutile, or less than 1 Ma at granulite facies conditions (Fig. 3). Zirconium re-equilibration at lower temperatures would require unrealistic cooling rates or thermal-overprinting durations, which again reinforces the suitability of the 550 °C filter as: a) a conservative approach that will only include low-T, low T/P rutile grains, and b) correspond to a real peak-T estimate under low dT/dP conditions, that has not been affected by either diffusion or recrystallisation processes under any realistic geological conditions.

As introduced earlier, only in rare circumstances rutile will form at lower than 10-13 kbar for $T < 550\text{ °C}$ (e.g. Luvizotto et al., 2009). Most frequently these are associated with more uncommon protoliths (MgO-rich or CaO-rich metapelites), to fluid-precipitates, and texturally prone not to survive well weathering (due to small size and aggregate-like texture;

Luvizotto et al., 2009). Therefore, any bias resulting from this filter (P of 13 kbar & < 100ppm Zr = 550 °C) strongly resides when pressures were higher and not lower than our assumption for rutile stability. This implies that we exclude potential low T/P rutile grains derived from higher temperature eclogite facies rocks. Also, this results in a mix in the field of “blueschist” between low-T eclogite and blueschist derived grains (grey field, Fig. 3). But by doing so, we increase the interval of confidence in this assessment, as we do not include false positives (such as grains formed at higher T/P conditions). If we were to use a different filter (pink star, Fig. 3), we could inevitably include more eclogite facies-derived grains (low T/P), but we would introduce uncertainty from potential HP amphibolite facies-derived grains (intermediate T/P).

A pressure of 13 kbar was applied to all grains in the dataset, and uncertainties on this selected pressure (2 kbar) are propagated in quadrature. We consider Zr measurement uncertainty, the calibration uncertainty, and the weighted mean average of the standard deviation of temperature calculated based on all rutile grains from single metamorphic rocks to calculate the final uncertainty (see below). Together, these should account for both Zr-in-rutile variability in natural rocks, and for the analytical uncertainties. A minimum 10-15 °C uncertainty in the calibration is reported from Kohn (2020), while in the literature there is a discussion of the effects on α -quartz activity in the temperature estimate that can amount to about 50-100 °C (that does not affect the metafelsic-derived grains). On average, the propagated natural variance uncertainty amounts to around 3%. We use this value (natural variance) to propagate uncertainties on each single-grain analysis as follows:

$$TZr_{rut} \pm = \sqrt{(natural\ variance)^2 + (Zr\ precision)^2 + (P \pm)^2}$$

By applying a 13 kbar pressure to the entire dataset, in order to better estimate the low temperature end, we bias most of the higher Zr concentrations in rutile towards the “amphibolite” facies conditions field (Fig. 3 – following the isopleths from eclogite facies conditions to 13 kbar). For example, a rutile grain that originally formed at 25 kbar containing

600 ppm Zr (750 °C), when recalculated at 13 kbar yields a 670 °C estimate and will plot in the intermediate T/P field (Fig. 3). The opposite occurs with low-P granulite rutile grains (< 10 kbar, formed under high T/P) when recalculated to 13 kbar. Yet, this P variance is restricted to ca. 5 kbar, and thus it might only account for a small T variation (sometimes enclosed within all the propagated uncertainties; < 30 °C; Fig. 3). Therefore, we do not discuss in any particular detail the variance seen in the high-grade metamorphic realm, as this variance reflects several competing factors, but it does indicate the presence of high-grade rutile and thus of high T/P.

4. ASSESSING THE METAMORPHIC RECORD BY UTILISING DETRITAL RUTILE

4.1. Detrital rutile grains nature: discriminating sources

As mentioned in section 1, rutile can grow after metamorphic reactions, in a wide range of bulk rock compositions, or associated to magmatic and fluid precipitating processes. To retrieve peak-T estimates from the Zr-in-rutile geothermometer, rutile grains were screened to assess the process by which they were formed. High field strength elements (HFSE), Sn and W can be used to distinguish some of these different rutile growth processes (Agangi et al., 2019; Pereira et al., 2019). Some key features of magmatic-related rutile include very high W, Sn, Sb and Nb concentrations (e.g. Meinhold et al., 2010; Agangi et al., 2019) or very high Nb/Ta ratios. Rutile is also known to form in ore mineralisation settings yielding very high Sb/V, Sn, Sb and W. Authigenic rutile and/or rutile related to low-T fluids yields low Nb/Ta ratios, as Ta becomes more compatible with rutile in the presence of aqueous fluids, combined with low Zr/Hf ratios (Pereira et al., 2019). Because published analyses of detrital rutile usually lack full trace element composition reporting, only a small fraction of the available U-Pb detrital rutile data could be included in this work.

While trace-element based discrimination diagrams are often sensitive to variations in protolith composition, in Agangi et al. (2019) data come from 8 samples, from 3 different

areas ($n_{\text{rut}} = 245$) and are combined with extensive published data, making it a rather comprehensive study. In Pereira et al. (2019), the fluid-related field is based on 3 samples from a single unit ($n_{\text{rut}} = 50$), presented together with data from another study reporting authigenic rutile and combined with published metamorphic rutile data ($n_{\text{tot}} = 453$). These boundaries might be broader than depicted in Figure 4, and future studies might better refine these. Still, by combining these different discriminating diagrams, we preclude, as most as possible, inclusion of low-T and -P rutile, as well as magmatic-related rutile grains.

Rutile grains from NW Scotland show no significant zonation or alteration, and they mostly lack inclusions. No inclusions of sulphides or extreme porosity were observed, such as commonly reported in rutile from ore deposit settings (Scott and Radford, 2007; Scott et al., 2011; Agangi et al., 2019; Pereira et al., 2019; appendix 4). Published studies also reported similar textures and included only chemically homogeneous grains. Trace element-based discrimination diagrams were applied to our dataset (Fig. 4). The majority of rutile grains yield Nb/Ta and Zr/Hf values commonly found in metamorphic settings, although a few grains yield very low or high Nb/Ta values (Fig. 4A). Most rutile grains yield Sn and W concentrations below 1000 ppm (Fig. 4B, C) and Sb values under 20 ppm (Fig. 4D). Some published data show Sn/Sb-W values compatible with magmatic-related or Au-mineralised sources. Generally, rutile grains included in this study have low Sb/V (Fig. 4C) suggesting that even when Sn-W are more elevated (Fig. 4B), the rutile grains are of a metamorphic origin (Fig. 4).

We excluded grains that plot in the *fluid-related* or *magmatic* fields, which reduced the dataset from 840 to 735 (appendix 2). Therefore, the resulting dataset includes only grains that grew from metamorphic reactions, and thus can be used to infer metamorphic conditions.

4.2. Low T/P metamorphic record

Each datapoint displayed on Figure 5 has been calculated using Kohn (2020) Zr-in-rutile combined equation and a pressure of 13 kbar, following the discussion in section 3. Despite the natural bias in assuming a given temperature, the uncertainties associated with it (discussed in section 3 and that for high T/P rocks it can amount to an overestimation of 30 °C) still allow us to draw conclusions regarding the existence of very high, moderately high or low temperature rutile. Rutile temperature data show periods with a wide range, separated by periods of more uniform growth temperatures (Fig. 5) that correspond to events within the supercontinental cycle (e.g. Brown and Johnson, 2019). Periods showing the widest variations in peak metamorphic temperatures occur between 0.3 and 0.55 Ga, 1.0 and 1.2 Ga, and 1.7 and 2.1 Ga, corresponding with periods of supercontinent assembly and collisional orogenesis. A significant number of detrital rutile yield temperatures above 850 °C, which despite the method used for its determination, are only compatible with rutile formed at granulite facies conditions. These take place during assembly of the Gondwana-Pangea, Nuna and Kenor supercontinents (Fig. 5).

Few rutile grains record peak temperatures lower than 550 °C ($n = 31$) or than 580 °C ($n = 62$), and the majority of these low T rutile are Phanerozoic in age (Fig. 5). Although the data offers no insight into the geothermal gradient at any particular time, as they overlap with the different T/P fields from (Brown and Johnson, 2018), we can directly link estimated peak temperatures with the geothermal gradient index (Fig. 5). These wide temperature variations are compatible with those described for paired metamorphic belts (Brown and Johnson, 2018), indicating quite different metamorphic grades in rocks of the same age. In the Carboniferous and in the Ediacaran where low and high T/P are known, our dataset shows evidence of low- and high- T rutile (and hence low and high T/P), tying together the metamorphic rock and rutile record, and reinforcing the suitability of this approach in probing earlier periods. From this small detrital rutile dataset, we obtained a few low T rutile grains between 1.0 and 1.2 Ga, and also between 1.7 and 2.2 Ga (Fig. 5). We note that those low T/P rutile grains have the same provenance as some of those derived from higher T/P .

Therefore, this new approach and dataset confirm the existence of low T/P and paired metamorphism during the late Palaeoproterozoic and late Mesoproterozoic, during both Nuna and Rodinia assembly, as well as in the Neoproterozoic to Palaeozoic during Gondwana and then Pangea assemblies. The number of cases recording Rodinia assembly are few in comparison to Gondwana-Pangea or Nuna, and they only record tectonometamorphic processes from the Grenville Province on east Laurentia (Pereira et al., 2020). U-Pb and Zr resetting of rutile have been reported in other studies (Zack and Kooijman, 2017) and show that Pb diffuses much faster than Zr. Full resetting of the U-Pb system in rutile in these cases would imply the existence of such conditions prior to the late Palaeoproterozoic. Indeed, a few rutile grains with ages between 2.3 and 2.55 Ga yield temperature estimates between 550 and 580 °C but not lower. No older, Archaean rutile grains selected in this study yield low- T indicative of a low T/P gradient (Fig. 5), but more data are required to confirm this observation.

Preservation Bias of the Exposed Metamorphic Crust and ‘Paired’ Metamorphism

In this new compilation of detrital rutile data, we have probed the sedimentary record in the search for low T/P metamorphism by applying the Zr-in-rutile geothermometer to detrital metamorphic rutile covering most of Earth’s history. We show that both low and high T/P conditions can be inferred since at least 2.1 Ga. The absence of Archaean rutile grains yielding < 550 °C is consistent with the absence of low T/P rocks of this age in the Archaean geological record (Brown and Johnson, 2019). Despite the relatively restricted number of low- T eclogite occurrences of Proterozoic age, our relatively small dataset show that these conditions prevailed. Thus, the lack of preserved blueschists and low- T eclogites prior to the Neoproterozoic represents a preservation bias that can be probably linked to retrogression and overprinting of HP-UHP units at suture zones and to the small stability fields of some indicator minerals (e.g. lawsonite). We argue that metamorphic rutile, preserved as detrital grains in the sedimentary record, can track low and high/intermediate T/P conditions through time. Applied to a given basin and using detrital grains of similar age, it can also provide the

missing evidence of paired metamorphic conditions over time, which is envisaged as a hallmark of sustained subduction zones in modern plate tectonics. Our data show that both during Rodinia and Nuna assemblies, rutile grains show this dual low and high T/P and thus that modern plate tectonics has been operating since at least the late Palaeoproterozoic, shaping and conditioning the evolution of the continental crust. Furthermore, the absence of low T/P conditions ($T < 550\text{ }^{\circ}\text{C}$) in the late Archean, both from the detrital rutile and rock records, suggests that contrasting mechanisms were operating during continental assembly at that time. However, some detrital rutile with late Archean, early Palaeoproterozoic age yield growth temperatures between 550 and 580 $^{\circ}\text{C}$, many of which are of metamafic affinity. In quartz-absent rocks, Zr will be preferentially taken by rutile, implying that by applying the Zr-in-rutile thermometer calibrated for $a_{\alpha\text{-quartz}} = 1$ we are overestimating the temperature. Since there is no other line of evidence to assist in $a_{\alpha\text{-quartz}}$ estimation at the time of rutile growth, we can not ascertain if these temperatures are overestimated, but it leads to an open possibility that low T/P subduction could have taken place at the end of the Archean. More detrital rutile data yielding those ages are thus required.

CONCLUSIONS

To investigate metamorphic conditions through time, we have looked at detrital rutile preserved in the sedimentary record as a tracer of past metamorphic conditions. Rutile yielding temperatures lower than 550-580 $^{\circ}\text{C}$ is linked to low T/P conditions, which together with very high temperature detrital rutile and the rock record can be used to infer the presence of paired metamorphic conditions and tectonic processes through time.

While the likely transition between early Earth geodynamics and the onset of subduction seems to have been diachronous as recorded on different cratons (Cawood et al., 2018; Laurent et al., 2014), we suggest that it is the youngest evidence of this transition that serves as evidence of a completed switch to modern plate tectonics, with an interconnected plate boundary system operating worldwide.

The period between the first onset of subduction between 3.2-3.0 Ga (Cawood et al., 2018; Dhuime et al., 2012) and the last appearance of a TTG to sanukitoid transition culminates at 2.13 Ga (Moreira et al., 2020, 2018). This final transition is marked by the first appearance of low T/P and paired metamorphism, as recorded by detrital rutile, in agreement with a few retro-eclogite occurrences with this age (see Brown et al., 2019 for references, and Holder et al., 2019). This transition is also manifested in the current crustal structure of several Palaeoproterozoic age belts, where recent seismological data is consistent with development of a palaeo-subduction network by ca. 2 Ga (Wan et al., 2020) and also with the oldest preserved linked linear orogenic belts of Eburnean age (Condie, 2013). Thus, although the metamorphic rock record is envisaged as supporting a major change in geodynamics at the dawn of the Phanerozoic after a protracted transition (Brown et al., 2020; Brown and Johnson, 2018; Stern, 2005), we contend that the preserved rock record indicates that the onset of modern plate tectonics took place during the late Palaeoproterozoic. By using sedimentary rocks as an archive of the continental crust we have started to contribute towards a more complete overview of the low T/P metamorphic conditions through time and of its forcing mechanisms.

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REFERENCES CITED

419 Agangi, A., Plavsa, D., Reddy, S.M., Olierook, H., Kylander-Clark, A., 2020. Compositional
420 modification and trace element decoupling in rutile: Insight from the Capricorn Orogen,
421 Western Australia. *Precambrian Res.* 345, 105772.
422 <https://doi.org/10.1016/j.precamres.2020.105772>

423 Agangi, A., Reddy, S.M., Plavsa, D., Fougereuse, D., Clark, C., Roberts, M., Johnson, T.E.,
424 2019. Antimony in rutile as a pathfinder for orogenic gold deposits. *Ore Geol. Rev.* 106,
425 1–11. <https://doi.org/10.1016/j.oregeorev.2019.01.018>

426 Angiboust, S., Harlov, D., 2017. Ilmenite breakdown and rutile-titanite stability in
427 metagranitoids: Natural observations and experimental results. *Am. Mineral.* 102,
428 1696–1708. <https://doi.org/10.2138/am-2017-6064>

429 Brown, M., Johnson, T., 2019. Time's arrow, time's cycle: Granulite metamorphism and
430 geodynamics. *Mineral. Mag.* 83, 323–338. <https://doi.org/10.1180/mgm.2019.19>

431 Brown, M., Johnson, T., 2018. Secular change in metamorphism and the onset of global
432 plate tectonics. *Am. Mineral.* 103, 181–196. <https://doi.org/10.2138/am-2018-6166>

433 Brown, Michael, Johnson, T., Gardiner, N.J., 2020. Plate Tectonics and the Archean Earth.
434 *Annu. Rev. Earth Planet. Sci.* 48, 1–30. [https://doi.org/10.1146/annurev-earth-081619-](https://doi.org/10.1146/annurev-earth-081619-052705)
435 [052705](https://doi.org/10.1146/annurev-earth-081619-052705)

436 Campbell, I.H., Squire, R.J., 2010. The mountains that triggered the Late Neoproterozoic
437 increase in oxygen: The Second Great Oxidation Event. *Geochim. Cosmochim. Acta*
438 74, 4187–4206. <https://doi.org/10.1016/j.gca.2010.04.064>

439 Carruzzo, S., Clarke, D.B., Pelrine, K.M., MacDonald, M.A., 2006. Texture, composition, and
440 origin of rutile in the South Mountain Batholith, Nova Scotia. *Can. Mineral.* 44, 715–729.
441 <https://doi.org/10.2113/gscanmin.44.3.715>

442 Cawood, P.A., Hawkesworth, C.J., Pisarevsky, S.A., Dhuime, B., Capitanio, F.A., Nebel, O.,

443 2018. Geological archive of the onset of plate tectonics. *Philos. Trans. R. Soc. A Math.*
 444 *Phys. Eng. Sci.* 376. <https://doi.org/10.1098/rsta.2017.0405>

445 Condie, K.C., 2013. Preservation and recycling of crust during accretionary and collisional
 446 phases of Proterozoic orogens: A bumpy road from Nuna to Rodinia. *Geosciences*,
 447 3(2), 240–261. <https://doi.org/10.3390/geosciences3020240>

448 Condie, K.C., 2018. A planet in transition: The onset of plate tectonics on Earth between 3
 449 and 2 Ga? *Geosci. Front.* 9, 51–60. <https://doi.org/10.1016/j.gsf.2016.09.001>

450 Cruz-Urbe, A.M., Feineman, M.D., Zack, T., Jacob, D.E., 2018. Assessing trace element
 451 (dis)equilibrium and the application of single element thermometers in metamorphic
 452 rocks. *Lithos* 314–315, 1–15. <https://doi.org/10.1016/j.lithos.2018.05.007>

453 Dhuime, B., Hawkesworth, C.J., Cawood, P.A., Storey, C.D., 2012. A Change in the
 454 Geodynamics of Continental Growth 3 Billion Years Ago. *Science* (80-.). 335, 1334–
 455 1337.

456 Dhuime, B., Hawkesworth, C.J., Delavault, H., Cawood, P.A., 2017. Continental growth seen
 457 through the sedimentary record. *Sediment. Geol.* 357, 16–32.
 458 <https://doi.org/10.1016/j.sedgeo.2017.06.001>

459 Flowerdew, M.J., Fleming, E.J., Morton, A.C., Frei, D., Chew, D.M., Daly, J.S., 2019.
 460 Assessing mineral fertility and bias in sedimentary provenance studies: examples from
 461 the Barents Shelf. *Geol. Soc. London, Spec. Publ.* SP484.11.
 462 <https://doi.org/10.1144/sp484.11>

463 François, C., Debaille, V., Paquette, J.L., Baudet, D., Javaux, E.J., 2018. The earliest
 464 evidence for modern-style plate tectonics recorded by HP–LT metamorphism in the
 465 Paleoproterozoic of the Democratic Republic of the Congo. *Sci. Rep.* 8, 1–10.
 466 <https://doi.org/10.1038/s41598-018-33823-y>

467 Ganne, J., De Andrade, V., Weinberg, R.F., Vidal, O., Dubacq, B., Kagambega, N., Naba,
 468 S., Baratoux, L., Jessell, M., Allibon, J., 2012. Modern-style plate subduction preserved
 469 in the Palaeoproterozoic West African craton. *Nat. Geosci.* 5, 60–65.
 470 <https://doi.org/10.1038/ngeo1321>

471 Gao, X.Y., Zheng, Y.F., Xia, X.P., Chen, Y.X., 2014. U-Pb ages and trace elements of
 472 metamorphic rutile from ultrahigh-pressure quartzite in the Sulu orogen. *Geochim.*
 473 *Cosmochim. Acta* 143, 87–114. <https://doi.org/10.1016/j.gca.2014.04.032>

474 Gonçalves, G.O., Lana, C., Buick, I.S., Alkmim, F.F., Scholz, R., Queiroga, G., 2019. Twenty
 475 million years of post-orogenic fluid production and hydrothermal mineralization across
 476 the external Araçuaí orogen and adjacent São Francisco craton, SE Brazil. *Lithos* 342–
 477 343, 557–572. <https://doi.org/10.1016/j.lithos.2019.04.022>

478 Hart, E., Storey, C., Bruand, E., Schertl, H.P., Alexander, B.D., 2016. Mineral inclusions in
 479 rutile: A novel recorder of HP-UHP metamorphism. *Earth Planet. Sci. Lett.* 446, 137–
 480 148. <https://doi.org/10.1016/j.epsl.2016.04.035>

481 Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A.,
 482 Birbaum, K., Frick, D.A., Günther, D., Enzweiler, J., 2011. Determination of reference
 483 values for NIST SRM 610-617 glasses following ISO guidelines. *Geostand.*
 484 *Geoanalytical Res.* 35, 397–429. <https://doi.org/10.1111/j.1751-908X.2011.00120.x>

485 Jochum, K.P., Willbold, M., Raczek, I., Stoll, B., Herwig, K., 2005. Chemical Characterisation
 486 of the USGS Reference Glasses and BIR-1G Using EPMA , ID-TIMS , ID-ICP-MS and
 487 LA-ICP-MS. *Geostand. Geoanalytical Res.* 29, 285–302. [https://doi.org/10.1111/j.1751-](https://doi.org/10.1111/j.1751-908X.2005.tb00901.x)
 488 [908X.2005.tb00901.x](https://doi.org/10.1111/j.1751-908X.2005.tb00901.x)

489 Kohn, M.J., 2020. A refined zirconium-in-rutile thermometer. *Am. Mineral.* 105, 963–971.

490 Kooijman, E., Smit, M.A., Mezger, K., Berndt, J., 2012. Trace element systematics in

491 granulite facies rutile: Implications for Zr geothermometry and provenance studies. *J.*
492 *Metamorph. Geol.* 30, 397–412. <https://doi.org/10.1111/j.1525-1314.2012.00972.x>

493 Kotková, J., Harley, S.L., 2010. Anatexis during high-pressure crustal metamorphism:
494 Evidence from garnet-whole-rock REE relationships and zircon-rutile Ti-Zr thermometry
495 in leucogranulites from the Bohemian Massif. *J. Petrol.* 51, 1967–2001.
496 <https://doi.org/10.1093/petrology/egq045>

497 Kusky, T., 2020. Plate tectonics in relation to mantle temperatures and metamorphic
498 properties. *Sci. China Earth Sci.* 63, 634–642. [https://doi.org/10.1007/s11430-020-](https://doi.org/10.1007/s11430-020-9597-5)
499 [9597-5](https://doi.org/10.1007/s11430-020-9597-5)

500 Laurent, O., Martin, H., Moyen, J.F., Doucelance, R., 2014a. The diversity and evolution of
501 late-Archean granitoids: Evidence for the onset of “modern-style” plate tectonics
502 between 3.0 and 2.5Ga. *Lithos* 205, 208–235.
503 <https://doi.org/10.1016/j.lithos.2014.06.012>

504 Laurent, O., Martin, H., Moyen, J.F., Doucelance, R., 2014b. The diversity and evolution of
505 late-Archean granitoids: Evidence for the onset of “modern-style” plate tectonics
506 between 3.0 and 2.5 Ga. *Lithos* 205, 208–235.
507 <https://doi.org/10.1016/j.lithos.2014.06.012>

508 Lenardic, A., 2018. The diversity of tectonic modes and thoughts about transitions between
509 them. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 376.
510 <https://doi.org/10.1098/rsta.2017.0416>

511 Li, X. hua, Wei, G., Shao, L., Liu, Y., Liang, X., Jian, Z., Sun, M., Wang, P., 2003.
512 Geochemical and Nd isotopic variations in sediments of the South China Sea: A
513 response to Cenozoic tectonism in SE Asia. *Earth Planet. Sci. Lett.* 211, 207–220.
514 [https://doi.org/10.1016/S0012-821X\(03\)00229-2](https://doi.org/10.1016/S0012-821X(03)00229-2)

515 Liou, J.G., Zhang, R., Ernst, W.G., Liu, J., McLimans, R., 1998. Mineral parageneses in the
516 Piampaludo eclogitic body, Gruppo di Voltri, western Ligurian Alps. Schweizerische
517 Mineral. und Petrogr. Mitteilungen 78, 317–335.

518 Lombardo, B., Rolfo, F., 2000. Two contrasting eclogite types in the Himalayas: Implications
519 for the Himalayan orogeny. J. Geodyn. 30, 37–60. [https://doi.org/10.1016/S0264-](https://doi.org/10.1016/S0264-3707(99)00026-5)
520 [3707\(99\)00026-5](https://doi.org/10.1016/S0264-3707(99)00026-5)

521 Luvizotto, G.L., Zack, T., Triebold, S., Von Eynatten, H., 2009. Rutile occurrence and trace
522 element behavior in medium-grade metasedimentary rocks: Example from the
523 Erzgebirge, Germany. Mineral. Petrol. 97, 233–249. [https://doi.org/10.1007/s00710-](https://doi.org/10.1007/s00710-009-0092-z)
524 [009-0092-z](https://doi.org/10.1007/s00710-009-0092-z)

525 Meinhold, G., Anders, B., Kostopoulos, D., Reischmann, T., 2008. Rutile chemistry and
526 thermometry as provenance indicator: An example from Chios Island, Greece.
527 Sediment. Geol. 203, 98–111. <https://doi.org/10.1016/j.sedgeo.2007.11.004>

528 Moreira, H., Seixas, L., Storey, C., Fowler, M., Lasalle, S., Stevenson, R., Lana, C., 2018.
529 Evolution of Siderian juvenile crust to Rhyacian high Ba-Sr magmatism in the Mineiro
530 Belt, southern São Francisco Craton. Geosci. Front. 9, 977–995.
531 <https://doi.org/10.1016/j.gsf.2018.01.009>

532 Moreira, H., Storey, C., Fowler, M., Seixas, L., Dunlop, J., 2020. Petrogenetic processes at
533 the tipping point of plate tectonics: Hf-O isotope ternary modelling of Earth's last TTG to
534 sanukitoid transition. Earth Planet. Sci. Lett. 551, 116558.
535 <https://doi.org/10.1016/j.epsl.2020.116558>

536 Pape, J., Mezger, K., Robyr, M., 2016. A systematic evaluation of the Zr-in-rutile
537 thermometer in ultra-high temperature (UHT) rocks. Contrib. to Mineral. Petrol. 171.
538 <https://doi.org/10.1007/s00410-016-1254-8>

539 Pereira, I., Storey, C., Darling, J., Lana, C., Alkmim, A.R., 2019. Two billion years of
 540 evolution enclosed in hydrothermal rutile: Recycling of the São Francisco Craton Crust
 541 and constraints on gold remobilisation processes. *Gondwana Res.* 68, 69–92.
 542 <https://doi.org/10.1016/j.gr.2018.11.008>

543 Pereira, I., Storey, C.D., Strachan, R.A., Bento dos Santos, T., Darling, J.R., 2020. Detrital
 544 rutile ages can deduce the tectonic setting of sedimentary basins. *Earth Planet. Sci.*
 545 *Lett.* 537, 116193. <https://doi.org/10.1016/j.epsl.2020.116193>

546 Province, B., Shield, F., Melnik, A.E., Skublov, S.G., Rubatto, D., Müller, D., Li, X., Li, Q.,
 547 Berezin, A. V, Herwartz, D., Machevariani, M.M., 2021. Garnet and zircon
 548 geochronology of the Paleoproterozoic Kuru-Vaara. *Precambrian Res.* 353, 106014.
 549 <https://doi.org/10.1016/j.precamres.2020.106014>

550 Reinhard, C.T., Planavsky, N.J., Gill, B.C., Ozaki, K., Robbins, L.J., Lyons, T.W., Fischer,
 551 W.W., Wang, C., Cole, D.B., Konhauser, K.O., 2017. Evolution of the global
 552 phosphorus cycle. *Nature* 541, 386–389. <https://doi.org/10.1038/nature20772>

553 Rösel, D., Zack, T., Boger, S.D., 2014. LA-ICP-MS U-Pb dating of detrital rutile and zircon
 554 from the Reynolds Range: A window into the Palaeoproterozoic tectonosedimentary
 555 evolution of the North Australian Craton. *Precambrian Res.* 255, 381–400.
 556 <https://doi.org/10.1016/j.precamres.2014.10.006>

557 Rösel, D., Zack, T., Möller, A., 2018. Interpretation and significance of combined trace
 558 element and U–Pb isotopic data of detrital rutile: a case study from late Ordovician
 559 sedimentary rocks of Saxo-Thuringia, Germany. *Int. J. Earth Sci.* 0, 0.
 560 <https://doi.org/10.1007/s00531-018-1643-5>

561 Şengün, F., Zack, T., Dunkl, I., 2020. Provenance of detrital rutiles from the Jurassic
 562 sandstones in the Central Sakarya Zone, NW Turkey: U-Pb ages and trace element
 563 geochemistry. *Chemie der Erde.* <https://doi.org/10.1016/j.chemer.2020.125667>

564 Skelton, A., Peillod, A., Glodny, J., Klonowska, I., Månbro, C., Lodin, K., Ring, U., 2019.
565 Preservation of high-P rocks coupled to rock composition and the absence of
566 metamorphic fluids. *J. Metamorph. Geol.* 37, 359–381.
567 <https://doi.org/10.1111/jmg.12466>

568 Spear, F.S., Wark, D.A., Cheney, J.T., Schumacher, J.C., Watson, E.B., 2006. Zr-in-rutile
569 thermometry in blueschists from Sifnos, Greece. *Contrib. to Mineral. Petrol.* 152, 375–
570 385. <https://doi.org/10.1007/s00410-006-0113-4>

571 Stern, R.J., 2005. Evidence from ophiolites, blueschists, and ultrahigh-pressure
572 metamorphic terranes that the modern episode of subduction tectonics began in
573 Neoproterozoic time. *Geology* 33, 557–560. <https://doi.org/10.1130/G21365.1>

574 Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-in-
575 rutile thermometer. *J. Metamorph. Geol.* 25, 703–713. <https://doi.org/10.1111/j.1525-1314.2007.00724.x>

577 Triebold, S., von Eynatten, H., Luvizotto, G.L., Zack, T., 2007. Deducing source rock
578 lithology from detrital rutile geochemistry: An example from the Erzgebirge, Germany.
579 *Chem. Geol.* 244, 421–436. <https://doi.org/10.1016/j.chemgeo.2007.06.033>

580 Triebold, S., von Eynatten, H., Zack, T., 2012. A recipe for the use of rutile in sedimentary
581 provenance analysis. *Sediment. Geol.* 282, 268–275.
582 <https://doi.org/10.1016/j.sedgeo.2012.09.008>

583 Tsujimori, T., Sisson, V.B., Liou, J.G., Harlow, G.E., Sorensen, S.S., 2006. Very-low-
584 temperature record of the subduction process: A review of worldwide lawsonite
585 eclogites. *Lithos* 92, 609–624. <https://doi.org/10.1016/j.lithos.2006.03.054>

586 Wan, B., Yang, X., Tian, X., Yuan, H., Kirscher, U., Mitchell, R.N., 2020. Seismological
587 evidence for the earliest global subduction network at 2 Ga ago. *Sci. Adv.* 6, eabc5491.

588 <https://doi.org/10.1126/sciadv.abc5491>

589 Weller, O.M., St-Onge, M.R., 2017. Record of modern-style plate tectonics in the
590 Palaeoproterozoic Trans-Hudson orogen. *Nat. Geosci.* 10, 305–311.
591 <https://doi.org/10.1038/ngeo2904>

592 Whitney, D.L., Davis, P.B., 2006. Why is lawsonite eclogite so rare? Metamorphism and
593 preservation of lawsonite eclogite, Sivrihisar, Turkey. *Geology* 34, 473–476.
594 <https://doi.org/10.1130/G22259.1>

595 Zack, T., Kooijman, E., 2017. Petrology and Geochronology of Rutile. *Rev. Mineral.*
596 *Geochemistry* 83, 443–467. <https://doi.org/10.2138/rmg.2017.83.14>

597 Zack, T., Moraes, R., Kronz, A., 2004a. Temperature dependence of Zr in rutile: Empirical
598 calibration of a rutile thermometer. *Contrib. to Mineral. Petrol.* 148, 471–488.
599 <https://doi.org/10.1007/s00410-004-0617-8>

600 Zack, T., von Eynatten, H., Kronz, A., 2004b. Rutile geochemistry and its potential use in
601 quantitative provenance studies. *Sediment. Geol.* 171, 37–58.
602 <https://doi.org/10.1016/j.sedgeo.2004.05.009>

603 Zerkle, A.L., 2018. Biogeodynamics: Bridging the gap between surface and deep Earth
604 processes. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 376.
605 <https://doi.org/10.1098/rsta.2017.0401>

606 Zhou, G., Fisher, C.M., Luo, Y., Pearson, D.G., Li, L., He, Y., Wu, Y., 2020. A clearer view of
607 crustal evolution: U-Pb, Sm-Nd, and Lu-Hf isotope systematics in five detrital minerals
608 unravel the tectonothermal history of northern China. *GSA Bull.* 1–15.
609 <https://doi.org/10.1130/b35515.1>

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Figure 1. **Comparison between temperature estimates based on Zr-in-rutile (Kohn, 2020) and on mineral equilibria** for 45 samples from 14 published studies (appendix 1). For Zr-in-rutile estimates, average Zr concentrations were used. Uncertainty on the Zr-in-rutile temperatures was calculated using mineral equilibria determined pressure variation and the Zr concentration standard deviation of each sample. A) correlation between both methods using average estimates; B) correlation between both methods adjusting the temperature estimate of mineral equilibria taking into account its variation from classical thermometry.

Figure 2. **Boxplot diagram** depicting temperature estimates based on single grain Zr-in-rutile (Kohn, 2020) for multiple samples (n=52), totalling 1123 rutile grains (appendix 1). Each Boxplot corresponds to a different sample, and data are coloured according to different metamorphic grade derived from the mineral assemblage. In cold colours, data derived from metamafic rocks, while warm colours from metafelsic rocks.

Figure 3. **Temperature-Pressure diagram** for Zr concentrations in rutile (isopleths in grey shades; Kohn 2020). In dashed blue, the minimum conditions for P-T path following low geothermal gradients, and in red, maximum for high geothermal gradients (from Palin et al., 2020). Orange lines correspond to the rutile-in reaction boundary in high silica system (granitoid composition similar to average pelite), the darker line corresponding to the most stable conditions at all given protolith compositions, while light orange to rutile occurrence under low CaO (1 wt%) compositions (from Angiboust and Harlov, 2017). The black line corresponds to the boundary of blueschist to eclogite facies conditions (from Palin et al., 2020). Yellow star corresponds to the intersection of low T/P minimum conditions with the rutile-in reaction and Zr isopleth. This defines for a 100 ppm Zr, at 13 kbar, 550 °C maximum temperature filter. The dashed black triangle highlights the range of conditions that are ignored by applying a temperature filter to the data, which would still be considered low T/P-related conditions. The brown dashed lines correspond to estimates of diffusivity of Zr in rutile (from Cherniak et al., 2007). Each line can be used to interpret the effects of cooling rate or timescales of thermal overprinting-induced diffusion for 200µm grain sizes (which corresponds to the average of observed grain sizes in our samples). Very slow (0.6 °C/Ma), slow (2.5 °C/Ma) or fast (75 °C/Ma) cooling rates of metamorphic terranes can lead to re-equilibration of Zr in rutile to equivalent concentrations of 600 °C, 650 °C or 800°C, respectively. Thermal overprinting events can lead to Zr diffusion if thermal regimes overprint at higher than 600 °C for more than 50Ma, than 650 °C if more than 10 Ma, and to 800°C for over 0.5 Ma. Pink star corresponds to conditions at which rutile could still be assigned as from T/P conditions, but with a lower level of confidence, if we also consider analytical/experimental uncertainties. The black field represents impossible high P, low-T conditions on Earth.

Figure 4. **Discrimination diagrams applied to detrital rutile** (data can be found in appendix 2); **a.** based on Zr/Hf and Nb/Ta from (Pereira et al., 2019) with discriminative fields for low-P fluid-related, metamorphic s.s. and peridotite-related rutile. **b.**, **c.**, and **d.** based on Sn and W, W an Sb/V, and Sb and W concentrations, respectively, from (Agangi et al., 2019) with discriminative fields for metamorphic *sensu stricto*, Au-mineralised related rutile and granitoid-related rutile. Symbols include measurement uncertainties as 1-sigma. Detrital rutile data used in this study to estimate temperatures plot within the metamorphic *sensu stricto* field of both diagrams. Dashed, red lines indicate filters applied for this discrimination.

Figure 5. The metamorphic record retrieved from the detrital archive; Metamorphic temperature estimates using the Zr-in-rutile geothermometer at 13 kbar (Kohn, 2020) versus detrital rutile U-Pb age; n = 735. For comparison, fields for low, high and intermediate T/P are plotted from (Brown and Johnson, 2018) and fields dividing temperature ranges for the different metamorphic facies (amph: amphibolite; ecl: eclogite; bs: blueschist; gs: greenschist). Dashed blue line corresponds to the new inferred field for low T/P based on both the detrital rutile and rock record. Yellow symbols correspond to $\log(\text{Cr/Nb}) < 0$ and Nb > 800 ppm (metafelsic; $a_{\alpha\text{-quartz}} = 1$) whereas blue symbols correspond to $\log(\text{Cr/Nb}) > 0$ or Nb < 800 ppm (metamafic; $a_{\alpha\text{-quartz}} = \text{unknown}$) following (Meinhold et al., 2008). Data sources can be found in the text. 1-sigma data uncertainties fall within the symbol used for plotting.

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Author's contributions: **IP** undertook sample collection and processing, SEM and LA-ICPMS work, data handling and interpretation, and has written the main parts of the manuscript. **CS** supervised the project and data processing, has discussed data interpretation, and substantively revised the manuscript. **JD** provided support during SEM and LA-ICPMS work. **HM** has been involved with data compilation, discussion and manuscript revision. **RS** and **PAC** have provided feedback and discussions related with the background research and have substantively revised the manuscript. All co-authors have contributed to the final version of this manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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