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^{207}Pb-excess in carbonatitic baddeleyite as the result of Pa scavenging from the melt

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Abstract

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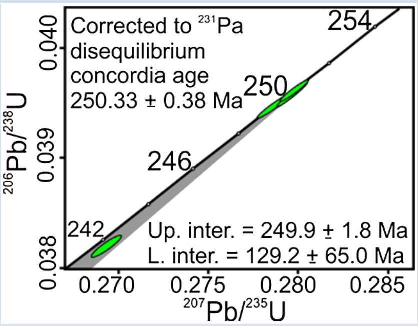

For the last two decades, the end of the voluminous phase of eruptions of the Siberian Traps large igneous province has been constrained by a U-Pb date of discordant baddeleyite collected from the Guli carbonatite intrusion with the assumption that the discordance resulted from unsupported ^{207}Pb. In this study we have re-analysed baddeleyite from the same intrusion and found two types of discordance: (1) due to ^{207}Pb-excess, and (2) radiogenic lead loss from high U mineral inclusions. The former implies that baddeleyite is an efficient scavenger of protactinium during crystallisation, leaving the magma depleted in this element. Together with a published high precision U-Pb date of 252.24 ± 0.08 Ma for the Arydzhansky Formation, our new date of 250.33 ± 0.38 Ma for the Guli carbonatite constrains the total duration of the voluminous eruptions of the Siberian Traps LIP at 1.91 ± 0.38 million years. The lower intercept of the (^{231}Pa)/(^{235}U) corrected discordance line yields a date of 129.2 ± 65.0 Ma, which points to the widespread Early Cretaceous rifting in East and Central Asia.

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Introduction

Precise ^{40}Ar/^{39}Ar and U-Pb dating has provided strong evidence for the rapidity of the most voluminous phase of large igneous province (LIP) magmatism. Such events typically last just a few million years or even less than a million years, although low volume eruptions may post-date voluminous magmatic pulses by ten or more million years (*e.g.*, Siberian Traps; Burgess and Bowring, 2015; Ivanov *et al.*, 2018a). The Siberian Traps LIP (Fig. 1a) is the most voluminous among Phanerozoic continental LIPs (Ivanov, 2007) and is considered as the cause of the most pronounced terrestrial Permian-Triassic mass extinction (Erwin *et al.*, 2002). Thus, the timing and duration of the Siberian Traps LIP are of particular interest for the Earth Sciences.

Nearly twenty years ago, Kamo *et al.* (2003) bracketed the voluminous phase of magmatism of the Siberian Traps LIP between the U-Pb dates of 251.7 ± 0.4 Ma and 250.2 ± 0.3 Ma. These dates were obtained, respectively, from perovskite in melanephelinite in the lowermost, so called Arydzhansky Formation, and baddeleyite from carbonatite, in the uppermost, so called Guli volcanic-intrusive complex (Fig. 1b,c). A stratigraphically consistent U-Pb date of 251.1 ± 0.3 Ma for zircon from trachyrhyodacite in the intermediate Delkansky Formation was also reported (Kamo *et al.*, 2003). The analytical method was at that time state of the art isotope dilution thermal ionisation mass spectrometry (ID-TIMS). A later determination of the age of the Arydzhansky and Delkansky Formations with high precision U-Pb ID-TIMS geochronology by Burgess and Bowring (2015), gave slightly older perovskite dates of 252.20 ± 0.12 Ma and 252.27 ± 0.11 Ma for the Arydzhansky Formation, and slightly older zircon dates of 251.901 ± 0.061 Ma and 251.483 ± 0.088 Ma for the Delkansky Formation (here errors are 2σ internal analytical for the reason explained below). Subsequent geochronology of the Guli carbonatites by Malich *et al.* (2015), using chemical microprobe dating of thorianite and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) dating of baddeleyite, obtained dates consistent with Kamo *et al.* (2003). The methods of Malich *et al.* (2015) were, however, unable to yield precisions better than ±1 Ma, at best, which is comparable with the expected total duration of the voluminous phases of LIP magmatism.

The reason to re-assess the Kamo *et al.* (2003) data is because the U-Pb results for the dated baddeleyite grains were discordant and the age was calculated from the ^{206}Pb/^{238}U ratio with the assumption that the discordance resulted from unsupported ^{207}Pb. In this study, we provide additional higher precision U-Pb ID-TIMS dating results on baddeleyite of the Guli carbonatite and discuss the relevance of the unsupported ^{207}Pb explanation.

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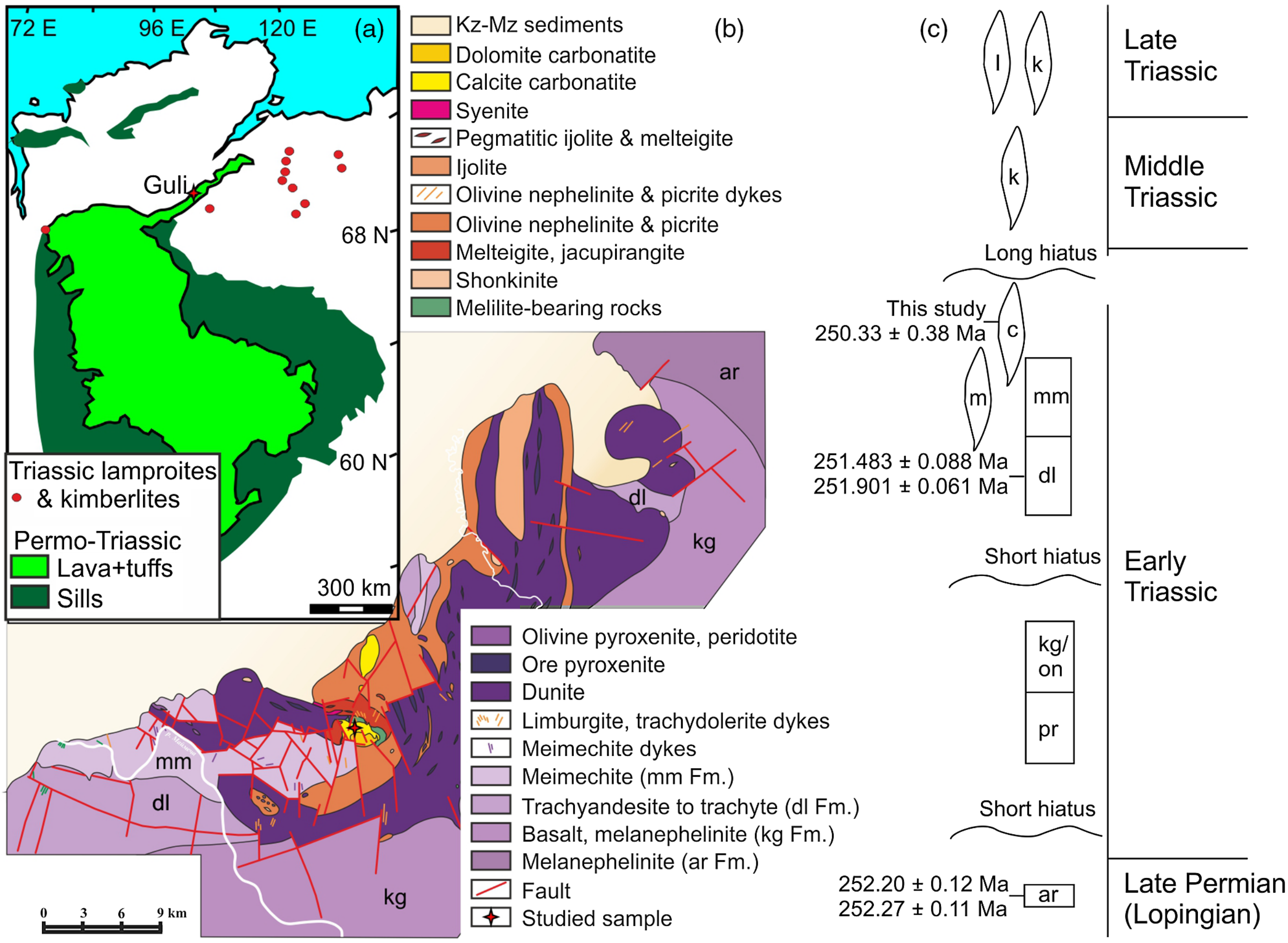

Figure 1 **(a)** Scheme of the Siberian Traps LIP (modified after Kogarko and Zartman, 2007). **(b)** Map of Guli volcanic-intrusive complex (Myshenkova *et al.*, 2020). **(c)** Generalised stratigraphic relationships between volcanic and intrusive units at the Meimecha-Kotuy region (Ivanov *et al.*, 2018b). High precision U-Pb dates are after Burgess and Bowring (2015) and this study (errors are 2σ analytical). Acronyms: ar – Arydzhansky Fm.; pr – Pravoboyarsky Fm.; kg/on – Kogotoksky Fm.; dl – Delkansky Fm.; mm – Meimechinsky Fm.; m – meimechite intrusions; c – carbonatite-bearing Guli complex; k and l – kimberlite and lamproite intrusions.

Geological Setting

The Guli complex is the largest alkaline-ultramafic complex on a global scale. It has an exposed area of about 470 km^2, but magnetic and gravimetric anomalies suggest an overall extension of 1500 km^2 (Egorov, 1991). The complex is composed of variable mafic alkaline and ultramafic rocks and carbonatites (Fig. 1b). Carbonatites form two stocks (named plugs in Kamo *et al.*, 2003), a southern and a northern one, each about 4.5 km^2 in size (Fig. 1b). The studied sample (GU-70) is from the southern stock. It is composed of calcite, apatite and magnetite, subordinate phlogopite and accessory baddeleyite. Apatite and magnetite form strips of different orientation (Fig. S-1). Baddeleyite is found as well formed crystals of dark brown colour up to 0.5 mm in size.

Methods

Baddeleyite grains and their mineral inclusions were imaged using an Alpha 300r confocal Raman spectrometer and scanning electron microscope (SEM) Hitachi SU-70 supplemented by an energy dispersive X-ray spectrometer of Oxford Instruments for chemical analysis. Apatite grains were analysed for $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios by LA-ICPMS on an Agilent 7900 quadrupole ICP-MS coupled to a Coherent COMPex Pro 110 utilising an ArF excimer laser operating at the 193 nm wavelength and a pulse width of ~20 ns. A RESOlution/ Laurin Technic S155 constant geometry ablation cell was used. Calibration of the $^{207}Pb/^{206}Pb$ ratio was done using analyses of the NIST610 reference glass analysed at the same conditions as the unknowns. Following the procedure of Thompson *et al.* (2016), the OD306 apatite was used as a primary in house geochronology reference material for calibration of Pb/U ratios and to correct for instrument drift. The Durango, McClure Mountain and 401 apatites were employed as secondary geochronology reference materials (Table S-1).

The baddeleyite grains processed for U-Pb dating were dark brown fragments, opaque to marginally translucent. They were first air abraded (Krogh, 1982), then cleaned in warm HNO_3 for 20 minutes and rinsed with H_2O and acetone. The grains were weighed and transferred to a Krogh-type teflon bomb, with the addition of HF and HNO_3 (12:1) and a ^{202}Pb-^{205}Pb-^{235}U spike. The spike composition has been harmonised with that of the EARTHTIME ET2535 spike (Corfu *et al.*, 2016) used by Burgess and Bowring (2015). Dissolution occurred at 195 °C for 5 days, followed by one night at 195 °C in 3N HCl, and chemical separation in ion exchange resin. The solution with Pb and U was loaded on outgassed Re filaments with silica gel

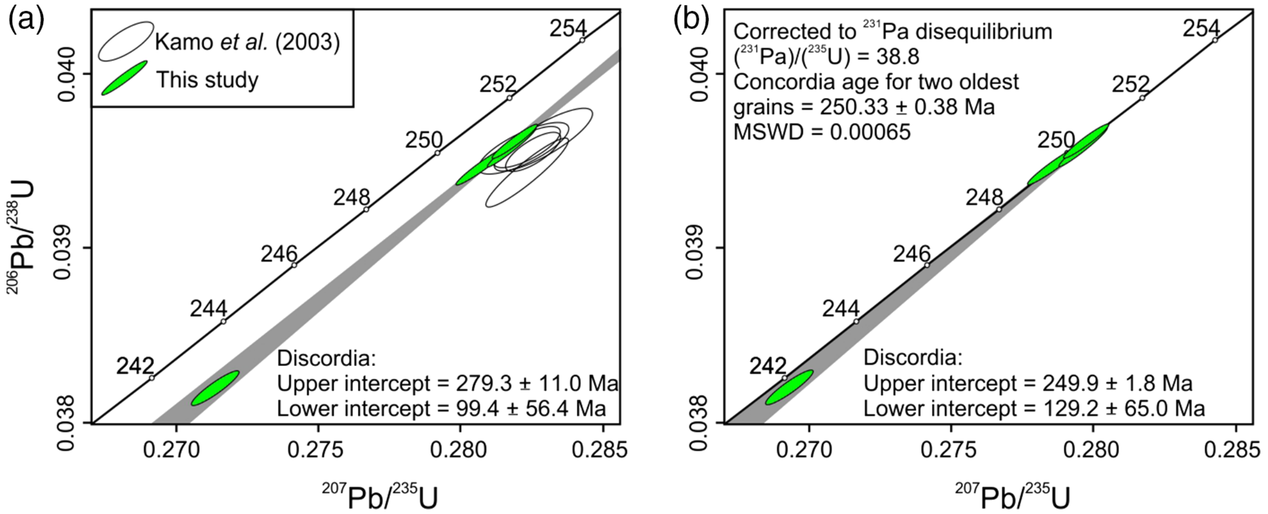

Figure 2 Concordia diagrams for Guli baddeleyite. **(a)** Green (new data), open symbols (Kamo *et al.*, 2003). **(b)** Data corrected for ^{231}Pa using decay constant of Jerome *et al.* (2020). The diagrams are plotted and ages calculated using IsoplotR (Vermeesch, 2018). Errors are 2σ analytical.

and H_3PO_4 and measured with a MAT262 mass spectrometer. Blank correction was 2 pg Pb and 0.1 pg U, the remaining common Pb was corrected using a composition calculated with the Stacey and Kramers (1975) model for the age of the sample (Table S-2). The ages were calculated using the decay constants of Jaffey *et al.* (1971) and $^{238}U/^{235}U = 137.88$, and were not corrected for ^{230}Th disequilibrium.

Results and Discussion

The results for the Guli baddeleyite are plotted in a concordia diagram together with those obtained previously by Kamo *et al.* (2003) (Fig. 2a). Three of the new analyses are clustered together close to previous analyses but the fourth is distinctly younger, indicating Pb loss. The reason for this behaviour is likely due to inclusions of another U-rich mineral as suggested by the higher level of U and initial Pb, and higher Th/U of this analysis (Table S-2). Such a mineral – Ta-Nb-Th-U-oxide was imaged by SEM (Fig. 3, Table S-3). Other common mineral inclusions are apatites (Figs. 3, S-2).

A discordia line can be drawn through the new, more precise data (Fig. 2a). It yields an upper intercept with concordia of 279.3 ± 11.0 Ma. However, this cannot reflect the true age of Guli carbonatite. It is too old relative to the date of thorianite (250.1 ± 2.9 Ma; Malich *et al.*, 2015) and to the host volcanic rocks (Fig. 1c).

All U-Pb data points are located to the right of concordia. This cannot be due to an incorrect correction of common lead because the ratio of radiogenic to common Pb is very high and, in addition, the initial $^{207}Pb/^{206}Pb$ in apatite, the most probable source of common lead in baddeleyite, is equal within uncertainty to that obtained with the Stacey and Kramers (1975) model (Fig. S-3). Thus, discordance of baddeleyite is real.

To explain such discordant baddeleyite data, Kamo *et al.* (2003) assumed unsupported ^{207}Pb, which accumulated from an excess of ^{231}Pa inherited by baddeleyite during its crystallisation from carbonatite magma. The ^{231}Pa-^{235}U disequilibrium required for the explanation of the discordant Guli baddeleyite data can be calculated as follows: the upper (^{231}Pa)/(^{235}U) value is constrained by the reasoning that the analyses should not be reversely discordant and the positive discordance cannot be such as to make the upper intercept of the discordia line older than the age of the Delkansky Formation (Fig. 1c). Using these constraints for the new, more precise data, (^{231}Pa)/(^{235}U) falls in the range between ~39.6 and 35.6. Assuming no loss of radiogenic lead for the two oldest grains and (^{231}Pa)/(^{235}U) = 38.8 (the value with the lowest MSWD) we obtain a concordia age of 250.33 ± 0.38 Ma (Fig. 2b). (Note: this age stays practically the same for a wide range of (^{231}Pa)/(^{235}U) values). Considering that the Nd isotope composition of Guli carbonatites ($\varepsilon Nd_T = +4.9$; Kogarko and Zartman, 2007) agrees only with that of meimechites (+4.5 to + 5.7; Ivanov *et al.*, 2018b), the age for the Guli baddeleyite may characterise the timing of emplacement of voluminous meimechite lavas.

Drawing a discordia line through the (^{231}Pa)/(^{235}U) corrected data yields the lower intercept age of 129.2 ± 65.0 Ma. This fits well with the timing of the Early Cretaceous large scale rifting event that occurred in the vast region of Central and East Asia (Wang *et al.*, 2011).

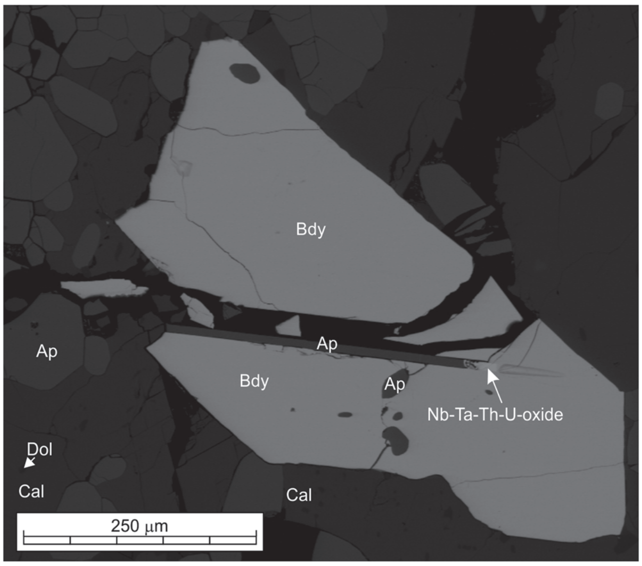

Figure 3 BSE image of a selected baddeleyite grain. Bdy – baddeleyite, Dol – dolomite, Cal – calcite, Ap – apatite, Nb-Ta-Th-U-oxide – unidentified phase (Table S-3).

The ^{231}Pa-^{235}U disequilibrium required for the explanation of the discordant Guli baddeleyite data by unsupported ^{207}Pb is not the largest among values suggested in other studies. For example, a study of Kovdor carbonatite-bearing massif suggests that (^{231}Pa)/(^{235}U) up to 100 can explain the discordance of baddeleyite data from this massif by unsupported ^{207}Pb (Amelin and Zaitsev, 2002). To our knowledge, only one study exists which analysed (^{231}Pa)/(^{235}U) directly in very young baddeleyite (Sun *et al.*, 2020). In that study, baddeleyite from Holocene syenite in the Vesuvius and Laacher See volcanoes requires (^{231}Pa)/(^{235}U) between 3 and 15. The most pronounced (^{231}Pa)/(^{235}U) suggested disequilibrium reaches 1,100 in zircon of Oligocene pegmatite in Pakistan's Himalaya (Anczkiewicz *et al.*, 2001).

The largest negative ^{231}Pa-^{235}U disequilibrium for igneous suites was recorded in the Oldoinyo Lengai volcano with (^{231}Pa)/(^{235}U) of ∼0.2 in carbonatite melts (Peate and Hawkesworth, 2005). In order to explain the positive and negative disequilibrium (^{231}Pa)/(^{235}U) values in baddeleyite and carbonatite melt, respectively, we need to accept that protactinium, compared to uranium, goes preferentially to baddeleyite, which is a typical early crystallising phase of carbonatites. No baddeleyite has ever been found in Oldoinyo Lengai natrocarbonatites, suggesting it could accumulate at the base of the magma chamber leaving the erupting carbonatite with low (^{231}Pa)/(^{235}U). Accumulation of baddeleyite agrees with the very low Zr concentrations in Oldoinyo Lengai natrocarbonatites (<32 μg/g) relative to associated silicate alkaline melts (>317 μg/g) (Simonetti *et al.*, 1997; Jung *et al.*, 2019).

Conclusions

Our new data concur with the idea that discordance of carbonatitic baddeleyite results from the presence of unsupported ^{207}Pb and agree with a previously published date for the Guli carbonatite by Kamo *et al.* (2003). A (^{231}Pa)/(^{235}U) of 39.6–35.6 is required to explain the discordant baddeleyite data. The high ^{207}Pb excess in baddeleyite implies that much protactinium is scavenged by crystallising baddeleyite, leaving the magma depleted in this element, as shown in carbonatitic magma such as at Oldoinyo Lengai. The total duration of the voluminous phase of the Siberian Traps LIP magmatism can be estimated from the period between the mean of two dates reported by Burgess and Bowring (2015) of 252.24 ± 0.08 Ma for the Arydzhansky formation and the preferred date of 250.33 ± 0.38 Ma for Guli carbonatite (errors are analytical because the two data sets are obtained with mutually homogenised isotopic tracers). This duration amounts to 1.91 ± 0.38 million years.

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Additional Information

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