Geology and geochronology of the Bynoe Pegmatite Field, with implications for lithium ore formation

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Introduction

Australia has a unique position in the global supply chain of lithium as the world's largest producer of the metal from hard rock resources. Most of this lithium is supplied from lithium–caesium–tantalum (LCT) pegmatite deposits in Western Australia. Recently however, exploration has realised the potential for the Northern Territory to supply the metal from the Bynoe Pegmatite Field, with mining operations by Core Lithium Ltd recently completed at the Grants lithium deposit.

Critical to the discovery of new LCT pegmatite deposits is an accurate understanding of the geological history and processes that lead to the formation of these rocks. At present there are two competing hypotheses for how LCT pegmatites form; the 'traditional' model invokes extensive fractional crystallisation of parental granitic intrusions to produce highly evolved and rare metal-rich residual liquids that then crystallised as pegmatites (eg London 2018). More recent models propose that these pegmatites form due to anatexis, followed by fractional crystallisation (eg Lv *et al* 2021). In the first case, pegmatite formation is spatially and temporally associated with a parental granite intrusion, whereas for the latter case temporal links to a granite pluton are not required. Therefore, constraining the timing of crystallisation of pegmatites within the context of the regional geology can be used to test these hypotheses, which then can inform exploration strategies for further mineralised pegmatite discoveries.

In this study we have undertaken *in situ* U–Pb dating of columbite/tantalite, cassiterite and apatite and *in situ* Lu–Hf dating of apatite, to accurately date the Grants deposit pegmatite. Dating of zircon was attempted, but these results proved highly discordant due to metamictisation (as is typical of pegmatitic zircons) and hence are not presented here. We present our results for columbite/tantalite, cassiterite and apatite, and discuss implications for the source of the greater Bynoe Pegmatite Field, including in the context of the crystal fractionation versus and anatectic models of LCT pegmatite formation.

Geological setting

The Bynoe Pegmatite Field is situated roughly 20 km south of Darwin in the Central Domain of the Pine Creek Orogen. The array of pegmatites – some LCT, some mineralisation-barren – extends approximately 200 km southwest. While

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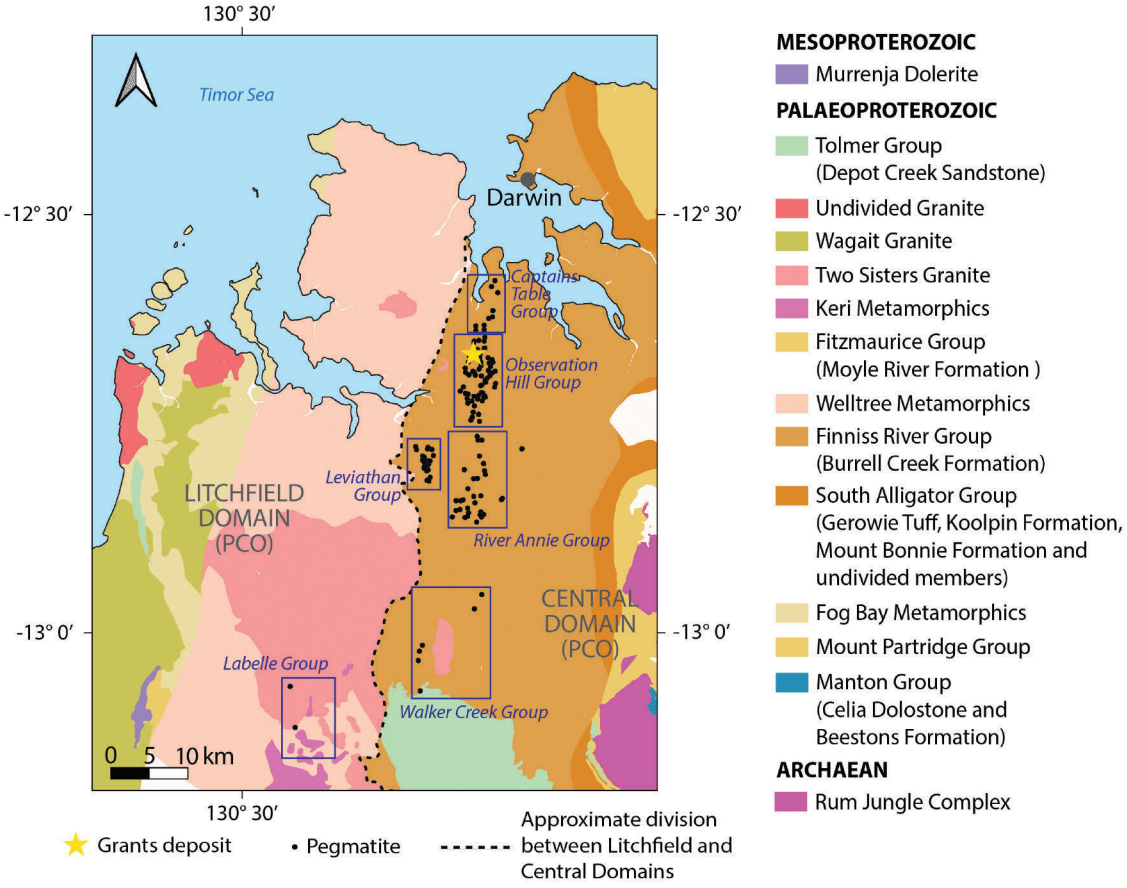

Figure 1. Regional geological map of the Bynoe Pegmatite Field with constituent groups of LCT pegmatites shown in italics.

most pegmatites were intruded into the Burrell Creek Formation of the Central Domain, some have intruded into the Welltree Metamorphics of the Litchfield Domain with the pegmatites being divided into six main groups (Captains Table Group, Observation Hill Group, Leviathan Group, River Annie Group, Walker Creek Group and Labelle Group) based in where they have clustered during emplacement (Rawlings 2017) (**Figure 1**). Ahmad (1995) provided some initial insights into the age of emplacement for the Bynoe pegmatites, recognising their undeformed nature and location in the contact aureole of the Two Sisters Granite, a peraluminous granite of the Alia Creek Suite that has been dated to ca 1850 to 1860 Ma (Page *et al* 1985, Worden *et al* 2008). Frater (2005) reported U–Pb ages of cassiterite and tantalite from the pegmatites within an age range of 1740–1720 Ma. These were interpreted as pegmatite crystallisation ages; however, these ages were obtained using techniques without matrix-matched standards, leading to some uncertainty regarding their accuracy.

Samples and geochronology methods

Apatite

Three large apatite crystals and 59 apatite grains obtained from rock crushing were analysed from drill core and hand sample specimens of the Grants deposit pegmatite provided by Core Lithium Ltd. The large apatite crystals are ~4 to ~6.5 mm wide, slightly fractured with a dark-blue to dark-green colouration and originate from the spodumene mineralised zone of the pegmatite. The 59 smaller apatite grains derive from a single sample of Grants deposit pegmatite after crushing the sample and sieving to between 430 µm and 250 µm. The sample was then panned to obtain a heavy mineral separate from which apatite grains were picked. These apatites were sky blue in colour and anhedral in shape, likely due to fracturing during sample crushing. The composition of the apatite was confirmed from scanning electron microscope energy dispersive X-ray spectroscopy (SEM EDS) analysis, with larger crystals then being mapped for Y content as a proxy for Lu (ie for suitability for Lu–Hf dating), using a Bruker M4 Tornado PLUS Micro-XRF spectrometer. This helped identify any zoning within the crystals and the optimal location for analysis via LA-ICP-MS.

The samples were analysed for their Lu–Hf and U–Pb isotopes using a Resonetics ArF 193 nm laser ablation system connected to an Agilent 8900x ICP mass spectrometer. Methods for determining Lu–Hf ages follow those outlined in Simpson *et al* (2021). The running conditions for Lu–Hf analysis included a beam size of 173 µm for larger crystals and 120 µm for smaller grains, with a laser fluence of 3.5 J/cm^2, and repetition rate of 10 Hz. The Bamble and Hr standards were used as the primary and secondary standards and gave calculated Lu–Hf ages of 1102 ± 5.5 and 356 ± 3 Ma respectively. These ages agree with previously reported ages of 1097 ± 5 Ma for the Bamble standard (Glorie *et al* 2024) and 361 ± 3.7 Ma for HR (Simpson *et al* 2021), demonstrating the accuracy of this method.

Apatite U–Pb analysis protocols included a 43 µm beam size, laser frequency of 5 Hz and fluence of 3.4 J/cm^2. The MAD apatite was used as a primary standard whilst the 401 and McClure Mountain apatite standards were used as the secondary standards. Analyses using the 401 and McClure Mountain apatite standards returned discordia lower intercept ages of 530 ± 8 Ma and 534 ± 8 Ma, respectively, which are broadly in agreement with the published age of 530.3 ± 1.5 Ma for the 401 apatite standard (Thompson *et al* 2016) and 523.5 ± 1.5 Ma for the McClure Mountain apatite standard (Schoene and Bowring 2006).

Cassiterite and columbite/tantalite

A total of 73 cassiterite grains and 80 columbite/tantalite grains from two Grants deposit pegmatite core samples were analysed for U–Pb isotopes. The grains were obtained by crushing the two samples before sieving and panning the samples to obtain a heavy mineral separate. The grains of columbite/tantalite and cassiterite were picked from these separates and mounted in epoxy resin mounts that were then polished to expose the grains. U–Pb analysis of both minerals was conducted at Adelaide Microscopy, a facility at The University of Adelaide using a Resonetics ArF 193 nm laser ablation system configured to an Agilent 7900x ICP mass spectrometer. For columbite/tantalite, the OXF columbite standard with a U–Pb age of 262.83 ± 0.29 Ma (Qing *et al* 2024), was used as the primary standard. A sample of Spargoville columbite served as an in-house secondary standard. The Spargoville columbite standard produced a weighted mean $^{207}Pb/^{206}Pb$ age of 2630 ± 4 Ma, falling within error of the reported age of 2627 ± 6 Ma (Kendall-Langley *et al* 2020), thus demonstrating the accuracy of this method. For cassiterite the Tabba Tabba cassiterite, with an age of 2838 ± 13 Ma (Denholm *et al* 2021), was used as the primary standard. Cassiterite from the Gaosong deposit of the Gejiu tin district was used as the secondary standard. The Gaosong cassiterite gave an age of 83 ± 1 Ma, falling within the reported age range of ~77 to ~83 Ma (Cheng *et al* 2019).

Results

Calculated ages from various mineral analysis routines using samples from the Grants deposit pegmatite include the following.

- Apatite returned a lower intercept (Wetherill diagram) U–Pb age of 1672 ± 27 Ma (n = 135), with a large MSWD of 5.7 (**Figure 2a**).
- Apatite gave a Lu–Hf isochron age of 1742 ± 5 Ma (n = 249), with a robust MSWD of 1.5 (**Figure 2b**).
- Cassiterite has a lower intercept U–Pb age (on Tera-Wasserberg concordia diagram) of 1757 ± 11 Ma (n = 51), with an MSWD of 2.4 (**Figure 2c**).
- Columbite/tantalite has an upper intercept (Wetherill diagram) U–Pb age of 1775 ± 34 Ma (n = 52; MSWD = 41) (**Figure 2d**). Some columbite/tantalite analyses show strong reverse discordance that may be caused by uranium-rich inclusions or uranium loss from metamict domains within the crystal lattice (Smith *et al* 2004). This dispersal is in part reflected by the very large MSWD, so this is considered an indicative age only.

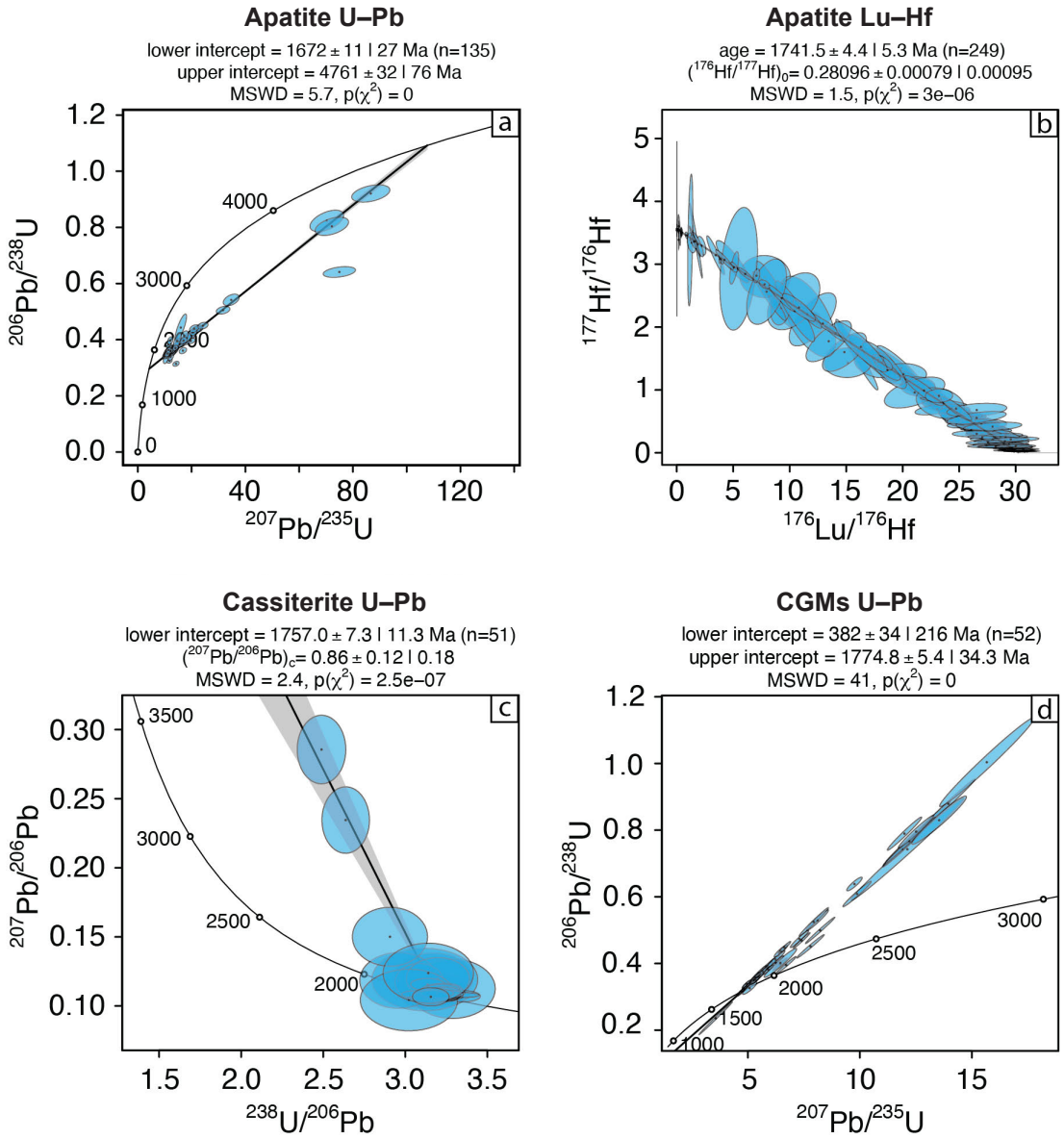

Figure 2. Geochronological results from LA-ICP-MS analysis of various minerals from the Grants deposit pegmatite. (**a**) Apatite via U–Pb. (**b**) Apatite via Lu–Hf. (**c**) Cassiterite via U–Pb. (**d**) Columbite group minerals (CGMs) via U–Pb.

Discussion

Interpretation of age data

The U–Pb apatite age determined here (1672 ± 27 Ma) is significantly younger than the Lu–Hf apatite age (1742 ± 5 Ma). The closure temperature of Lu–Hf in apatite is expected to be between 660°C and 730°C (Glorie *et al* 2024), which is likely higher that the pegmatite crystallisation temperature (McCaffrey and Jowitt 2023) and is significantly higher than the closure temperature of the U–Pb system in apatite (350–570°C; Glorie *et al* 2024). Indeed, the U–Pb apatite age is comparable to previously determined Ar–Ar ages for muscovite from the Bynoe pegmatites dated to ca 1700 to 1680 Ma (Frater 2005), which likely also has a similar closure temperature. Due to this, we interpret the Lu–Hf isochron age for apatite as representing the timing of primary crystallisation of apatite, and hence the pegmatites, whilst the U–Pb age is interpreted as recording a cooling age or a younger, separate thermal event.

Closure of the U–Pb system in cassiterite is considered to be well over 600°C (Zhang *et al* 2011). Therefore, our cassiterite U–Pb age is also interpreted to reflect pegmatite crystallisation age, although with a large MSWD it may be considered less reliable that the Lu–Hf apatite age. Our columbite/tantalite age data suffer from reverse discordance, and returned an extreme MSWD, meaning this age is considered indicative only. Collectively, we consider the crystallisation age of the Grants deposit pegmatite to be ca 1740 Ma, which is broadly consistent with previous U–Pb tantalite and cassiterite ages of ca 1745 to 1720 Ma (Frater 2005).

Implications for pegmatite formation

The ca 1740 Ma formation age for the Grants deposit pegmatite (and other Bynoe pegmatites) postdates, by

more than 100 my, the emplacement of the nearby Two Sisters Granite, which was previously suggested to be the parental magmatic source of the pegmatites (Rawlings 2017). This ca 100 my period is far too long to consider the Two Sister Granite and the pegmatites to have a direct crystal fractionation relationship. Instead, there may be another currently unrecognised intrusive body from which the pegmatites were derived, or the pegmatites may have an anatectic origin. The timing of pegmatite formation occurs just after the 1770 to 1780 Ma Shoobridge Event and therefore may have formed in response to post-orogenic anatexis or may relate to a prolonged period of sustained high geothermal gradients that allowed episodic crustal melting, as has been suggested for other Proterozoic terranes of Australia (eg Walsh *et al* 2015). Work is ongoing to further refine the geochronologic and tectonic history of the local geology, including the Bynoe Pegmatite Field.

Acknowledgements

The authors would like to thank Core Lithium Ltd and the Northern Territory Geological Survey for providing samples used in this research and for co-funding this research project. We would also like to thank Sarah Gilbert from Adelaide Microscopy for her expertise and assistance in collecting the LA-ICP-MS data.

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