

Article

Monazite as an Exploration Tool for Iron Oxide-Copper-Gold Mineralisation in the Gawler Craton, South Australia

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Abstract: The chemistry of hydrothermal monazite from the Carrapateena and Prominent Hill iron oxide-copper-gold (IOCG) deposits in the IOCG-rich Gawler Craton, South Australia, is used here to define geochemical criteria for IOCG exploration in the Gawler Craton as follows: Monazite associated with IOCG mineralisation: La + Ce > 63 wt% (where La > 22.5 wt% and Ce > 37 wt%), Y and/or Th < 1 wt% and Nd < 12.5 wt%; Intermediate composition monazite (between background and ore-related compositions): 45 wt% < La + Ce < 63 wt%, Y and/or Th < 1 wt%. Intermediate monazite compositions preserving Nd > 12.5 wt% are considered indicative of Carrapateena-style mineralisation; Background compositions: La + Ce < 45 wt% or Y or Th > 1 wt%. Mineralisation-related monazite compositions are recognised within monazite hosted within cover sequence materials that directly overly IOCG mineralisation at Carrapateena. Similar observations have been made at Prominent Hill. Recognition of these signatures within cover sequence materials demonstrates that the geochemical signatures can survive processes of weathering, erosion, transport and redeposition into younger cover sequence materials that overlie older, mineralised basement rocks. The monazite geochemical signatures therefore have the potential to be dispersed within the cover sequence, effectively increasing the geochemical footprint of mineralisation.

Keywords: monazite; exploration geochemistry; IOCG; Gawler Craton



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1. Introduction

Heavy mineral phases preserved within sedimentary cover sequence materials that overlie mineralised basement rocks have been demonstrated to be useful in mineral exploration (e.g., [1–5]). Heavy mineral phases may include monazite, zircon or oxide minerals such as ilmenite and rutile. The presence of heavy minerals in cover sequence materials may be used as an indicator for buried prospective basement rocks (e.g., [5–7]). The chemistry of heavy, resistate mineral phases may also be used as an indicator for mineralisation. For example, [8] showed that zircon chemistry can be used as a pathfinder for porphyry Cu ± Mo ± Au systems using Eu/Eu* and (Eu/Eu*)/Y ratios.

The Gawler Craton in South Australia is a poorly exposed region that is highly prospective for iron oxide-copper-gold (IOCG) deposits and hosts major mineralisation including the Olympic Dam, Prominent Hill and Carrapateena IOCG deposits (Figure 1). Ref. [3] demonstrated that the chemistry of the resistate mineral phase, monazite, in the Prominent Hill IOCG deposit in the Gawler Craton is elevated in light rare earth elements (LREEs) and depleted in Y and Th compared to igneous and metamorphic monazite from

the same district. This chemistry is also preserved in monazite from within younger glacial sediments that overlie the mineralised basement rocks, indicating that the chemistry of monazite can withstand processes of weathering, erosion, transport and sedimentation. However, the exploration criteria developed by [3] have only been tested on the Prominent Hill IOCG deposit, and not on other IOCG deposits within the Gawler Craton. Therefore, the applicability of these exploration criteria to searching for buried IOCG mineralisation in the broader Gawler Craton is unknown. The ability to apply the exploration criteria is of significance as the Gawler Craton is highly prospective for additional IOCG mineral deposits (e.g., [9]).

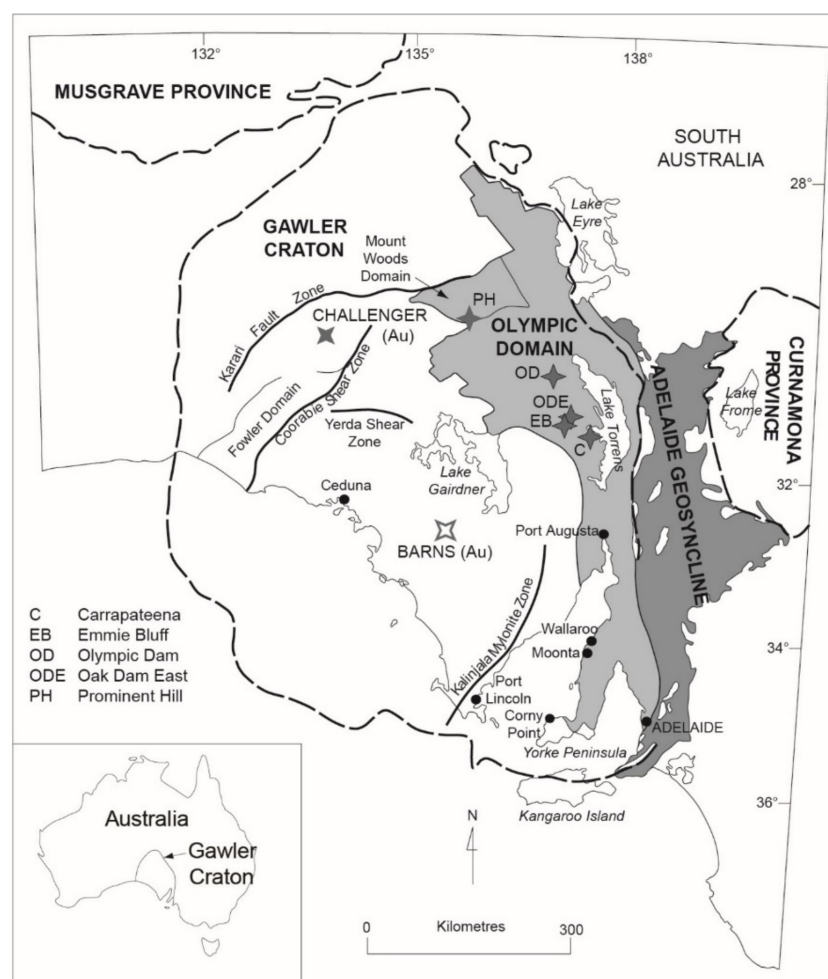


Figure 1. Geological map of the Gawler Craton showing the location of the IOCG-rich Olympic Domain as well as selected major deposits including Olympic Dam, Prominent Hill and Carrapateena. After [3].

In this paper, we present trace and rare earth element geochemistry for monazite in the Carrapateena IOCG deposit of the Gawler Craton, South Australia. We illustrate the differences in element composition of monazite from two distinct geological zones at Carrapateena: IOCG mineralised basement rocks and cover rocks over the deposit. Comparison of the chemistry of the Carrapateena monazite to monazite elsewhere in the Gawler Craton is made, with reference to monazite derived from the Prominent Hill IOCG deposit. We discuss the effect of transforming the chemistry data according to compositional data analysis techniques to consider effects of closure. The implications of using the monazite geochemical criteria in the exploration for IOCG deposits in the Gawler Craton is assessed and discussed.

2. Background

The Gawler Craton has undergone a protracted geological history from the Archean through to the Proterozoic [9–11]. The ca. 1600–1590 Ma evolution of the Gawler Craton is marked by a major episode of IOCG mineralisation [9,10]. IOCG mineralisation includes the giant Olympic Dam deposit and significant mineralisation in the Prominent Hill and Carrapateena deposits (Figure 1). Mineralisation is hosted within the Olympic Domain (Figure 1), which is considered highly prospective for additional IOCG deposits [9]. The challenge for explorers in the Gawler Craton is that it is overlain by extensive Neoproterozoic to Phanerozoic cover sequences [12,13]. Basement rocks are rarely exposed; the regional distribution of rock types, stratigraphy and structures are largely inferred from geophysical data [14,15] and the available samples are from sparsely distributed drill holes [16,17]. To be useful in this context, a geochemical exploration technique will tend to have the following characteristics [3,6,18–21]:

- The sample medium will be widespread (commonly intersected by drilling), easy to recognise and easy to sample.
- The analytical technique will be robust, reliable and repeatable.
- The geochemical criteria for recognising altered or mineralised rocks from ‘background’ will be unambiguous.
- The geochemical signal will extend beyond the zone of economic mineralisation and thus increase the exploration footprint of mineralisation.
- The processes responsible for the geochemical signal, both primary (e.g., hydrothermal alteration) and secondary (e.g., physical or chemical dispersion), are understood.

Ref. [3] demonstrated that hydrothermal monazite from the ca. 1585 Ma Prominent Hill IOCG deposit [22] in the Gawler Craton meet these criteria. The hydrothermal monazite preserves a unique geochemical signature, characterized by elevated LREEs and depleted Y and Th, compared to igneous and metamorphic monazite from the same district. Monazite with this chemistry is also found within the widespread Permo-Carboniferous glacial cover sediments that overlie the Prominent Hill deposit. The monazite chemistry provides a ‘scaled’ exploration ranking with potential for regional vectoring and target prioritisation. Monazite with $\text{La} + \text{Ce} > 63 \text{ wt\%}$ and Y and Th $< 1 \text{ wt\%}$ were shown to have similar chemistry to monazite derived from the Prominent Hill orebody and were therefore considered ‘compelling’. Monazite grains containing concentrations of $57.5 \text{ wt\%} < \text{La} + \text{Ce} < 63 \text{ wt\%}$ are considered ‘interesting’, and concentrations of $\text{La} + \text{Ce} < 57.5 \text{ wt\%}$ are considered ‘background’. The unique geochemical signature of monazite was used to develop a series of exploration criteria for whole-rock geochemical data using La and Ce content and $\text{La} + \text{Ce}/\text{Y}$ and $\text{La} + \text{Ce}/\text{Th}$ ratios for cover sequence materials, assuming that all LREE within the cover sequence samples are host within monazite. Whole-rock geochemical results showing $\text{La} > 75 \text{ ppm}$ and $\text{Ce} > 155 \text{ ppm}$ are considered anomalous. $(\text{La} + \text{Ce}):\text{Y}$ and $(\text{La} + \text{Ce}):\text{Th}$ ratios greater than 30:1 and 32:1, respectively, are considered ‘compelling’. ‘Interesting’ results are those where $(\text{La} + \text{Ce}):\text{Y}$ ratios are between 10:1 and 30:1 and $(\text{La} + \text{Ce}):\text{Th}$ ratios are between 16:1 and 32:1 [3]. The whole-rock geochemical criteria were used to map out compelling and interesting signatures within the glacial sediments. Ref. [3] demonstrated that the geochemical footprint of the Prominent Hill deposit within the glacial cover sequence materials is 2–3 times larger than the orebody itself. The geochemical signature is dispersed to the north of the deposit, which was the direction of movement of the Permian glacier.

The Carrapateena Deposit

The Carrapateena deposit is located in the central Olympic Domain (Figure 1) at the intersection of an interpreted major NNE-trending structure and a NW-trending fault corridor [23,24]. IOCG mineralisation is hosted within variably deformed quartz granite and quartz diorite of the Donnington Suite that yields an age of $1857 \pm 6 \text{ Ma}$ [23–29]. IOCG mineralisation occurs as steeply-dipping high grade bornite-dominant bodies surrounded by lower grade chalcopyrite-dominated mineralisation (Figure 2) and is hosted

within hematite-silica-sericite breccias that contain clasts of granite, gneiss and vein quartz. Chlorite/hematite breccias and volcano/sedimentary breccias are also recognised proximal to mineralisation. Alteration assemblages are dominated by hematite, chlorite and sericite with localised silica and siderite/ankerite alteration. Accessory minerals include barite, monazite, anatase, magnetite, apatite, fluorite and zircon. Cu mineralisation is disseminated or within veins or blebs and occurs as chalcopyrite, bornite and lesser covellite and chalcocite. Felsic and mafic dykes locally intrude the basement rocks [23–28]. Other mineralisation is also recognised in the local area including Khamsin and Fremantle Doctor [25,27].

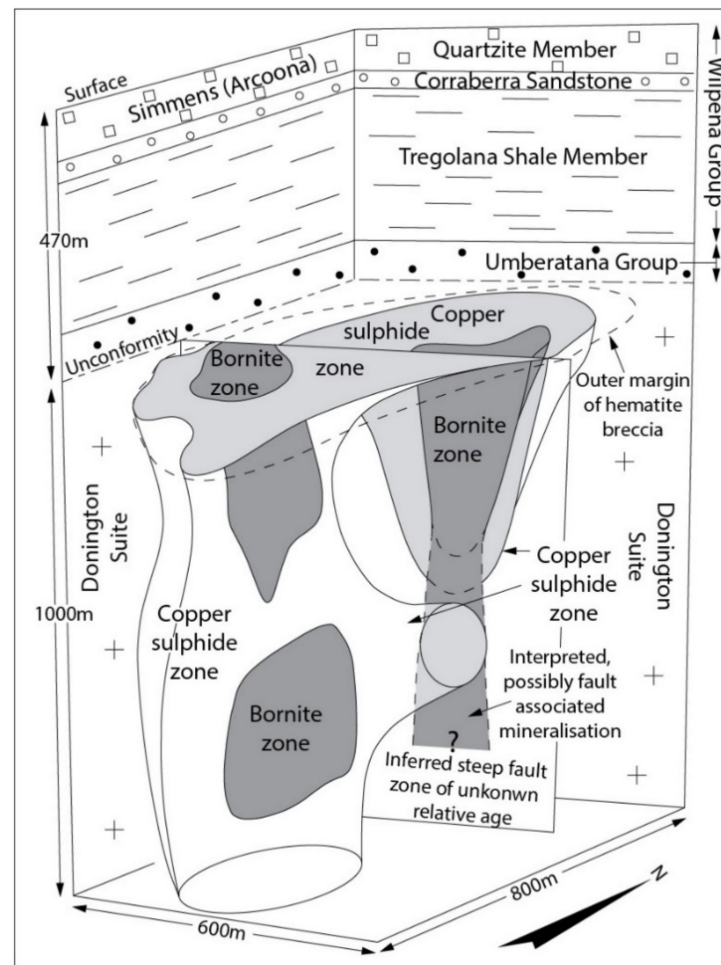


Figure 2. Schematic section of the Carrapateena IOCG deposit and overlying cover sequence materials of the Umberatana Group and Wilpena Group. After [26].

An approximately 470 m thick sequence of cover sediments unconformably overlies the mineralised Donnington Suite basement rocks in the Carrapateena area (Figure 2). The cover sediments are generally recognised as representing the Umberatana Group and Wilpena Group [23,26,28–31] that are Marinoan in age (ca. 650–635 Ma) [13,32]; however, it is noted that there are no absolute age dates available for the cover sequence materials that directly overlie the Carrapateena deposit. The basement/cover unconformity is marked by an approximately 10 m thick basal conglomerate that comprises a fine-grained matrix hosting well-rounded granitic, volcanic, quartz and hematite clasts [23,26,28,31]. The lowermost cover sequence rocks comprise variably gritty siltstones to sandstones with minor interbeds of dolomite. This whole package of rocks was assigned to the Whyalla Sandstone [23] and has since been divided into the Angepena Formation (~40 m of shales and siltstones) at the base, overlain by the Rynella siltstone (~30 m thick) and with ~10 m of dolostones of the Nucleleena Formation at the top [31]. No matter the division, the

rock package is accepted to represent the Umberatana Group. The Umberatana Group sediments are overlain by Wilpena Group sediments that include dark red-brown shale of the Tregolana Shale Member (formerly the Woomera Shale Member) (~270–300 m thickness), which is in turn overlain by ~25–40 m thick purple-brown, medium- to fine-grained sandstone of the Cooraberra Sandstone. The uppermost unit is a coarse-grained quartzite of the Simmens (Arcoona) Quartzite Member (~90 m thickness), which is exposed throughout the region [23,26,30,31].

3. Methodology

3.1. Sampling

All thirteen samples used in this study were collected from drill core (Figure 3; Table 1). Two samples were collected from mineralised basement rock within the Carrapateena deposit. Eleven samples were taken from the basal conglomerate of the cover sequence directly overlying the Carrapateena deposit. Conglomerate samples were selected to target a range of clast types including hematite breccias, altered granite, granite and volcanics. Cover samples were taken from 0–5 m above the basement–cover interface. All samples were prepared into thin sections and used for petrological and mineral chemistry analysis.

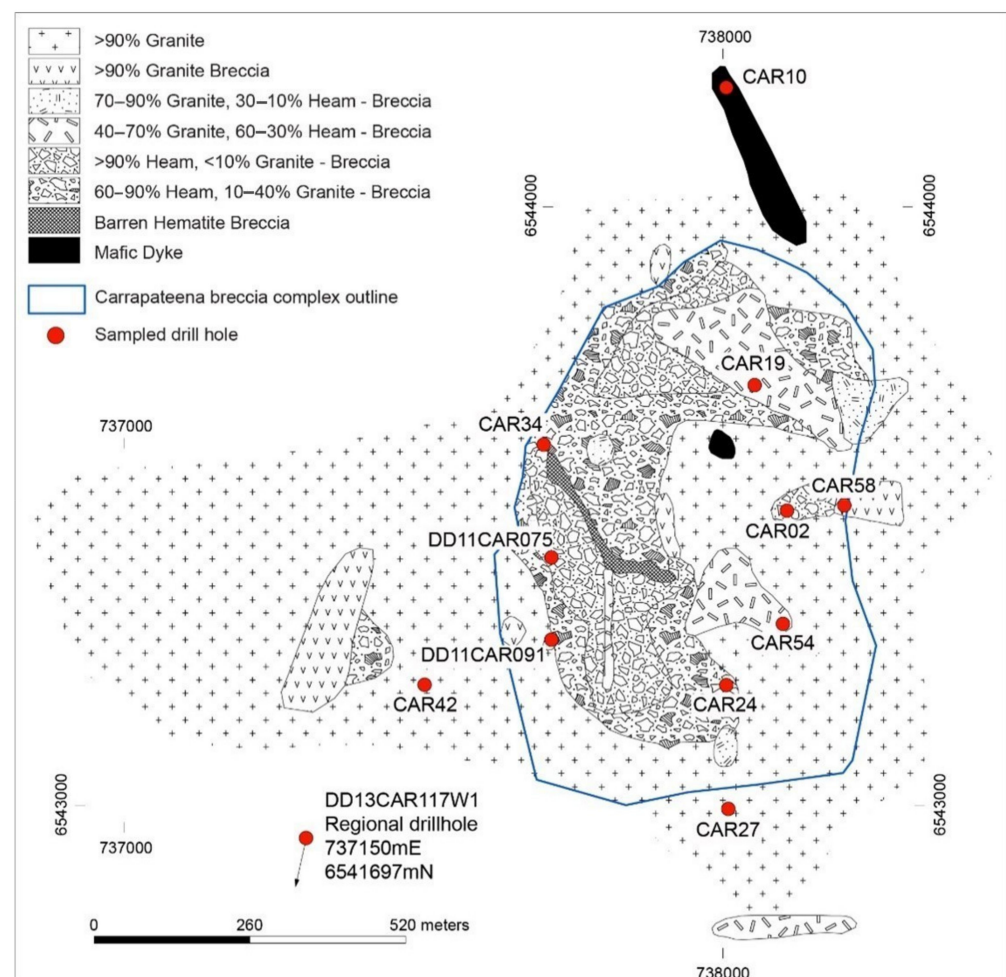


Figure 3. Top of basement geological map of the Carrapateena deposit showing the location of sampled drill holes. Location of the Carrapateena deposit is shown in Figure 1. Modified from [33].

Table 1. Details for samples taken across the Carrapateena deposit and used in this study. Includes DH name, sample number, depth from, depth to, basement/cover sample, basic mineralogical description, clast types for the conglomerate samples.

Hole ID	Sample ID	From (m)	To (m)	Lithological Description			Accessory Phases	
Drill holes sampled for mineralised basement rock								
CAR002	CAR002_627m	627.55	627.65	Hematite-quartz breccia, contains abundant chalcopyrite and pyrite with lesser bornite and minor molybdenite and sphalerite.			Monazite: abundant, typically subhedral to anhedral, up to 350 μm size, contain hematite and chalcopyrite inclusions. Other: apatite and florencite.	
DD11CAR075	CAR075_651m	651	651.4	Mineralised sandstone, contains disseminated bornite with pyrite typically completely enclosed within bornite.			Monazite: occurs as inclusions within quartz grains and as microgranular aggregates intergrown with hematite.	
Hole ID	Sample ID	From (m)	To (m)	Basement-Cover Interface (m)	Sampled Interval (m)	Lithological Description (From Sample Thin Section)	Accessory Phases	
						Matrix		Clast descriptions
Drill holes sampled for cover sequence basal diamictite								
CAR010	FIA_CAR010_01	458	458.3	458.6	0.3	Matrix supported, poorly sorted, polymictic diamictite. Matrix: angular to subangular sand-sized quartz and feldspar in a variably Fe-oxide-, calcite- or sericite-rich cement.	Pebble to cobble size; subangular to subrounded granite (~80–90%), rounded volcanics (~5%), rounded sandstone (<5%).	Monazite: anhedral, microgranular aggregates or whole grains in chlorite-altered granite and volcanic clasts and in the matrix. Other: Zircon and rutile dominate accessory phase budget; xenotime forms thin rims around zircon grains.
CAR019	FIA_CAR019_10	467.24	467.54	470.25	2.71	Very poorly sorted diamictite. Matrix: coarse-grained quartz- and feldspar-rich in a Fe-oxide-rich cement. Porous.	Large pebble-size angular hematite-rich clasts (~95%) and lesser granule to small pebble-sized sericite-altered volcanics (~5%).	Monazite: single, anhedral grain with a pitted surface was observed in a hematite-rich clast. Other: Accessory phases within hematite-rich clasts are dominated by apatite, florencite, zircon and rutile often intergrown with hematite and quartz.
CAR024	FIA_CAR024_21	486.52	486.87	488.63	1.76	Poorly sorted, polymictic, clast-supported diamictite. Matrix: sand-sized quartz and feldspar in a calcite cement with localised Fe-oxide near grain margins.	Sand to pebble size; well-rounded granite (~50%), volcanics and sediments (~20%), quartz/feldspar (~15%), subangular hematite-rich rock and hematite breccia (~10%) and mafics (~5%).	Monazite: not very abundant, only three grains identified and within hematite-rich and granite clasts. Other: Zircon, apatite and xenotime are common within hematite-rich clasts.

Table 1. Cont.

Hole ID	Sample ID	From (m)	To (m)			Lithological Description	Accessory Phases
CAR027	FIA_CAR027_05	491.65	491.9	492	0.1	Poorly sorted, matrix-supported diamictite. Matrix: sand-sized angular quartz in a sericite-rich or Fe-oxide-rich cement.	Angular granule- to pebble-sized granite clasts and large (~1.5 cm) rounded hematite-rich clasts. Monazite: only observed as within hematite-rich clasts, commonly subhedral with some monazite occurring as microgranular aggregates intergrown with hematite.
CAR034	FIA_CAR034_28	477	477.4	478.1	0.7	Moderately sorted, clast-supported diamictite. Matrix: fine-grained, quartz-dominated with a clay-rich cement with Fe-oxide rims around grain margins. Porous.	Granule to cobble size; rounded to subrounded volcanics (~65%), sandstone (~15%), hematite-rich rock and granite (<5%); subrounded to subangular K-feldspar and quartz grains (~15%). Monazite: No monazite grains observed in this sample. Other: Accessory phases are dominated by zircon, rutile and apatite.
CAR042	FIA_CAR042_36	478	478.3	483	4.7	Poorly sorted, clast-supported interval of diamictite approximately 7–8 m above the basement-cover interface. Selected as the clast population is dominated by hematite breccia that shows jigsaw fit textures. Noted that the clast population surrounding the sample site is dominated by cobble to boulder sized, well-rounded granite. Matrix: Quartz-dominated in a calcite cement.	Sample is dominated by a large pebble to cobble size, hematite-breccia clast that itself contains small pebble-sized subangular clasts of siltstone. Hematite breccia clasts are subangular, comprise ~45% of the clast population. Other clasts include rounded to subangular volcanics (~25%), rounded mafics with feldspar phenocrysts that are altered to sericite and leucoxene (~15%) and subrounded to subangular granite (~15%). Monazite: Scarce, only two monazite grains were identified, both were within quartz grains and have euhedral to subhedral shape. Other: Florencite is the dominant REE-baring phase within hematite-breccia clasts, apatite and rutile are the most commonly observed accessory phases within the sample.
CAR054	FIA_CAR054_20	489.8	489	489	0	Poorly sorted, clast-supported diamictite. Matrix: Fe-oxide rich cement.	Granule to cobble size; rounded to subangular quartzite (60%), hematite-rich clasts (~20%), immature sandstone clasts (arkose) (~15%), volcanics and granite (~5%). Monazite: Abundant within hematite-rich clasts and the matrix, typically euhedral to anhedral, often with inclusions of hematite or as microgranular aggregates intergrown with hematite. Other: zircon, xenotime, barite.

Table 1. Cont.

Hole ID	Sample ID	From (m)	To (m)			Lithological Description	Accessory Phases
CAR058	FIA_CAR058_14	467.4	467.6	469.6	2	Moderately sorted, polymictic, matrix- to clast-supported diamictite. Matrix: medium-grained quartz sand in a quartz cement.	Mostly granule to small pebbles with some large pebbles. Rounded to subangular quartz (40%), sericite altered microcline (25%), rounded volcanics (15%), subrounded to subangular granite (15%), rounded siltstone (<5%) and angular hematite-rich clasts (<2%). Monazite: occurs within granite, feldspar and hematite-rich clasts. In granite and feldspar, monazite is typically euhedral, up to 100 µm length. In hematite-rich clasts monazite occasionally occurs as microgranular aggregates intergrown with hematite. Other: Florencite occurs within hematite-rich clasts, is porous, often intergrown with and contains inclusions of hematite. Xenotime and zircon are present.
DD11CAR075	FIA_CAR075_31	491.1	491.26	492.5	1.24	Moderately sorted, clast-supported, polymictic diamictite. Matrix: quartz and K-feldspar rich.	Granule to large pebble size, angular to subrounded. Hematite breccia (~35%) and hematite-quartz-rich clasts (~35%), granite (~15%), siltstone/clay (~10%), volcanics (~5%). Monazite: abundant, typically within hematite-quartz-rich and volcanic clasts and within the matrix, anhedral to euhedral grains, also occurs as microgranular aggregates intergrown with hematite. Other: Florencite observed only within hematite-quartz-rich clasts, commonly euhedral, also occurs as anhedral inclusions within large monazite grains and as microscopic inclusions within hematite. Zircon and xenotime also observed.
DD12CAR091	FIA_CAR091_34	538.8	539	539	0	Moderately sorted, polymictic, clast-supported diamictite. Matrix: Fine-grained quartz in a calcite cement.	Medium pebble to cobble size. Dominated by rounded to subangular hematite-rich clasts (~90%) with lesser rounded chlorite- and sericite-altered granite (~10%). Monazite: commonly observed within clasts. Monazite within hematite-rich clasts is typically subhedral to euhedral and up to 130 µm size. Within altered granite clasts monazite is commonly microgranular aggregates up to 600 µm size, occur with numerous zircon and rutile grains.
DD13CAR117W1	FIA_CAR117W1_38	694	694.2	695.2	1	Poorly sorted, polymictic, clast-supported diamictite. Matrix: dominantly quartz within a carbonate (dolomite to ankerite) cement.	Granule to large pebble size. Dominated by subangular quartz grains (~45%), subrounded granite (~30%), angular to subrounded hematite-rich clasts (~10%), rounded sericite-altered mafics (~5%) and minor rounded volcanic, sandstone and dolomite clasts (~10%). Monazite: largely within hematite-rich clasts, subhedral to anhedral, intergrown with hematite and quartz. Other: Florencite and apatite commonly observed in hematite-rich clasts. Florencite is typically microporous and intergrown with hematite, locally forms rims and embayments around apatite. Rutile (also intergrown with hematite in hematite-rich clasts) and zircon.

3.2. Petrological Analysis and Element Mapping

Thin sections were carbon-coated and imaged using a Zeiss Merlin FEG SEM Cross-beam 540 at the University of South Australia. Operation parameters include a 20 kV accelerating voltage, 3 nA probe current and a working distance of 5.1–10 mm. Secondary electron (SE) imaging in conjunction with electron dispersive spectroscopy (EDS) was used to identify REE-bearing phases, including monazite.

3.3. Mineral Chemistry

Quantitative mineral chemistry of REE-bearing phases was collected using a Cameca SX5 electron microprobe (EPMA) equipped with 5 tuneable wavelength-dispersive spectrometers at Adelaide Microscopy, University of Adelaide. PeakSite v6.2 software was used for microscope operation and Probe was used as the EPMA software (distributed by Probe Software Inc., Eugene, OR, USA) for all data acquisition and processing. Combined operating conditions were utilised for each individual spot so that major and mobile elements were analysed first at 15 kV/20 nA followed by analysis of remaining low-level elements at 15 kV/100 nA. A 2 µm spot size was used for all analyses. The full list of elements analysed, and primary and interference standards and detail of chemistry calculation are presented in Appendix A.

3.4. Compositional Data Analysis

In [3], X-Y scatter plots of elements were used to illustrate the distinction between different compositional groups of monazite in the Carrapateena area. Because compositional data (such as multi-element geochemistry) are subject to closure (i.e., all components must add up to 100% [34,35]), we need to check that the data patterns identified in [3] do not contain artefacts resulting from closure. As there are three critical elements that distinguish the three compositional groups, these can be plotted on a ternary plot, which eliminates the closure problem. However, samples that contain low values of elements and plot near the boundaries of the ternary plot are compressed very close to each other by the nature of the ternary plot, making it hard to distinguish similar groups of samples. Scatter plots that use the isometric log ratio (ILR) transform are used to overcome this problem [36].

The structure of an ILR transform is simple to derive from a ternary plot. Three dependant variables (i.e., they add up to a fixed value) are transformed into two independent variables (no fixed sum constraint). Standard statistical techniques, such as calculating correlation, can only be applied to independent variables. In other words, three elements are transformed into two log ratios. The first log ratio can be chosen from one of the edges of the ternary plot (an edge is the line joining two vertices) and the second log ratio is the line perpendicular to the edge which joins the edge to the third vertex (Figure 4). For example, if the ternary plot has vertices Ce, La and Y, then the first log ratio uses the ratio between Ce and La, and the second log ratio is between Y and combined Ce and La. There are three possible choices of log ratio using different combinations of the three elements (Figure 4). The trends of the data can be used to select the most useful of the possible combinations. The isometric log ratios for Figure 4 are calculated as follows:

$$ILR_{La-Ce} = \sqrt{\frac{1}{2}} \cdot \log \frac{La}{Ce}$$

$$ILR_{Y-LaCe} = \sqrt{\frac{2}{3}} \cdot \log \frac{Y}{\sqrt{La \cdot Ce}}$$

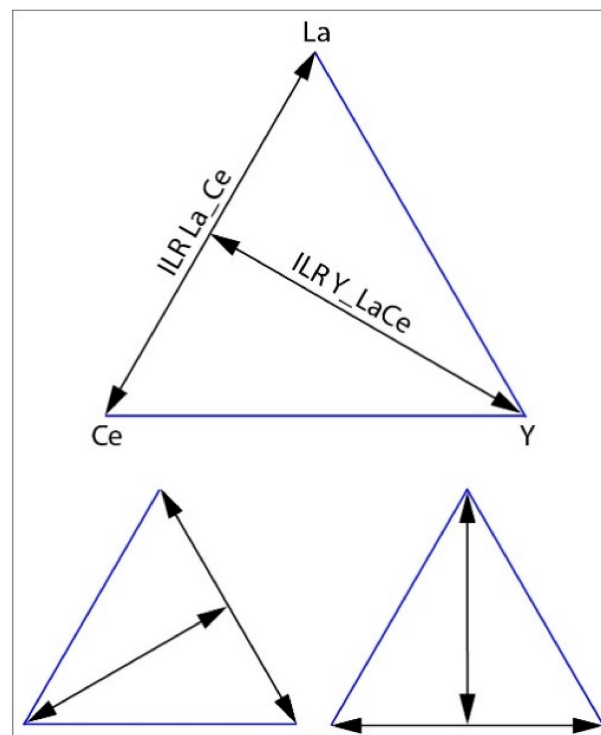


Figure 4. A ternary plot can be used as a guide for selecting log ratios where the (sub-)composition involves three elements. This plot shows different methods for selecting two independent variables. The two independent variables can be used to produce XY scatter plots.

4. Results

4.1. Sample Descriptions

Detailed descriptions for basement and cover sequence samples used in this study are given in Table 1. Locations of sampled drill holes are given in Figure 3.

Basement samples comprise a hematite-quartz breccia and a mineralised sandstone. Both samples preserve visible sulphides including chalcopyrite, pyrite, bornite, molybdenite and sphalerite.

Cover sequence samples are comprised of basal conglomerate and diamictite. Clast lithology is variable between samples and includes hematite-rich rock, unaltered and altered granite and volcanics, sediments and mafic rock as well as large quartz and K-feldspar grains. Clast shape ranges from angular to rounded. The dominant clast type is hematite-rich rock, which is often angular to subrounded (Table 1). The matrix is generally a fine- to medium-grained sand in a carbonate cement. The basal cover sequence sampled in this study is herein collectively termed diamictite due to the preservation of clasts of variable shape (angular to rounded).

4.2. Imaging Analysis

Representative BSE images are shown in Figure 5.

Monazite within mineralised basement rock samples occurs as euhedral to anhedral grains, commonly preserving inclusions of hematite and occasionally chalcopyrite. Microgranular aggregates of monazite with hematite inclusions were observed in one sample (DD11CAR075_651m).

Monazite grains from diamictite cover sequence samples were dominantly observed within hematite-rich clasts with lesser grains observed within volcanic, chlorite $\pm$ sericite altered granite clasts, granite clasts and as inclusions within quartz grains. Monazite was also observed within the diamictite matrix. Monazite is euhedral to subhedral within hematite-rich and granitic clasts, and euhedral to anhedral within the matrix. Additionally, monazite grains within hematite-rich clasts are often intergrown with, or contain inclusions

of, hematite and occur as microgranular aggregates. Monazite grains within the matrix less frequently contain inclusions of hematite. Microgranular aggregates of monazite intergrown with zircon and chlorite occur within granite clasts.

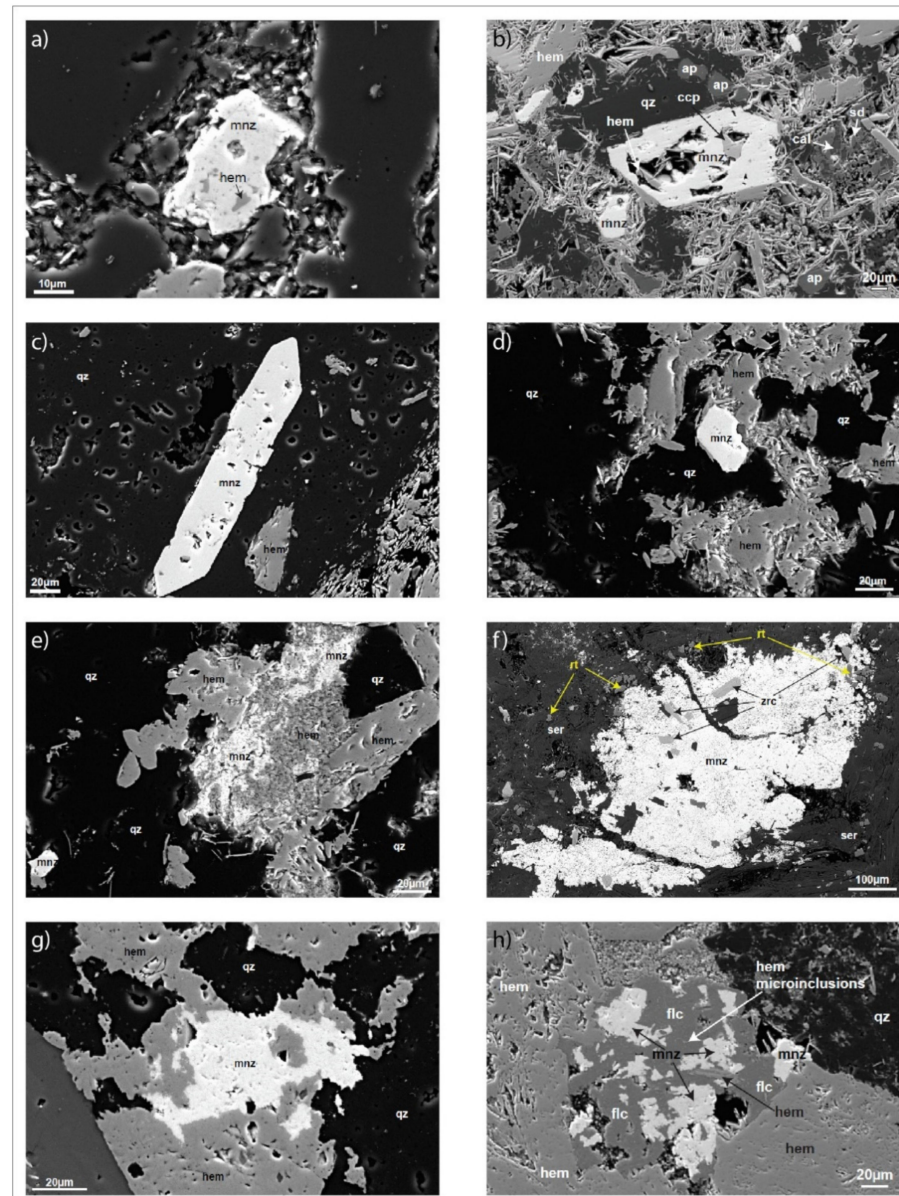


Figure 5. Representative SEM images of REE-bearing phases within basement and cover sequence samples in the Carrapateena deposit. (a) Euhedral monazite grain within a quartz grain in a hematite-rich clast (FIA_CAR091_34). (b) Euhedral monazite grain with hematite and chalcopyrite inclusions (CAR002_627). (c) Monazite grain containing hematite inclusions and preserved within the diamicctite matrix (FIA_CAR054_20). (d) Subhedral monazite grain within a hematite-quartz rich clast (FIA_CAR027_05). (e) Microgranular aggregates of monazite intergrown with hematite in a hematite-quartz rich clast (FIA_CAR027_05). (f) Microgranular monazite intergrown with zircon and rutile in a granite clast (FIA_CAR091_34). (g) Microgranular monazite intergrown with hematite (FIA_CAR058_14). (h) Large, anhedral monazite grains completely enclosed within florencite. Monazite and florencite preserve hematite inclusions and are preserved within a hematite breccia clast (FIA_CAR075_31). All images are secondary electron (SE) images. Sampled drillholes shown in Figure 3. Sample descriptions given in Table 1. Abbreviations: ap, apatite; cal, calcite; ccp, chalcopyrite; flc, florencite; hem, hematite; mnz, monazite; qz, quartz; rt, rutile; ser, sericite; sd, siderite; zrc, zircon.

4.3. Mineral Chemistry

Monazite chemistry is shown in Figures 6 and 7 and summarised in Table 2. All data are given in Supplementary Materials Table S1. Data from monazite in the basement and cover can be split into groups according to La, Ce, Nd, Y and Th chemistry (Table 2).

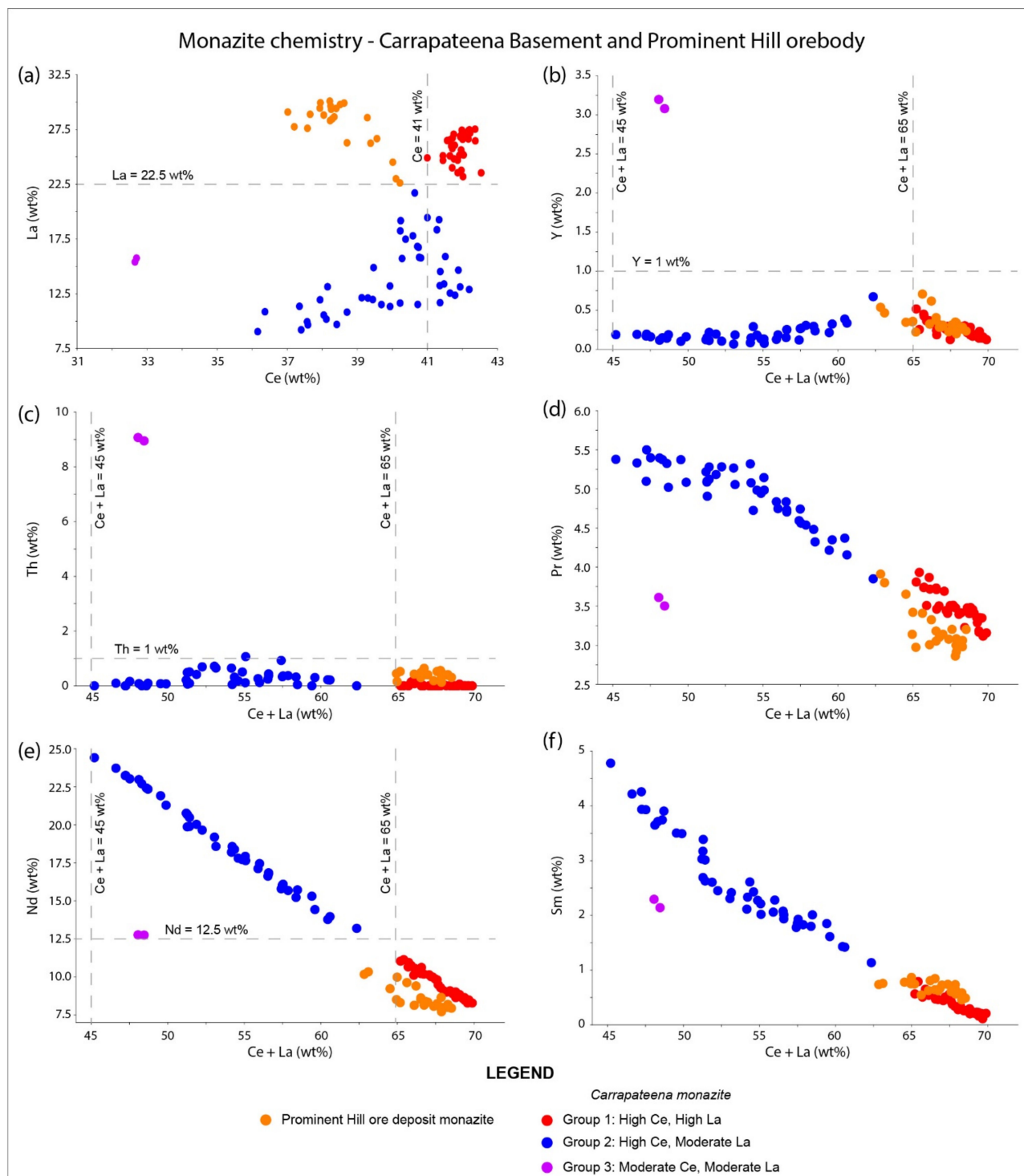


Figure 6. Geochemical plots for monazite from the Carrapateena basement samples and the Prominent Hill deposit. (a) Ce vs. La; (b–f): Ce + La vs. (b) Y; (c) Th; (d) Pr; (e) Nd; and (f) Sm. Thresholds defining Group 1 and Group 2 basement monazite are shown in (a–f). $ILRLa_Ce = \sqrt{\frac{1}{2}} \times \log\left(\frac{La}{Ce}\right)$; $ILRNd_LaCe = \sqrt{\frac{1}{2}} \times \log\left(\frac{Nd}{\sqrt{La \times Ce}}\right)$. Data for the Prominent Hill orebody taken from [3].

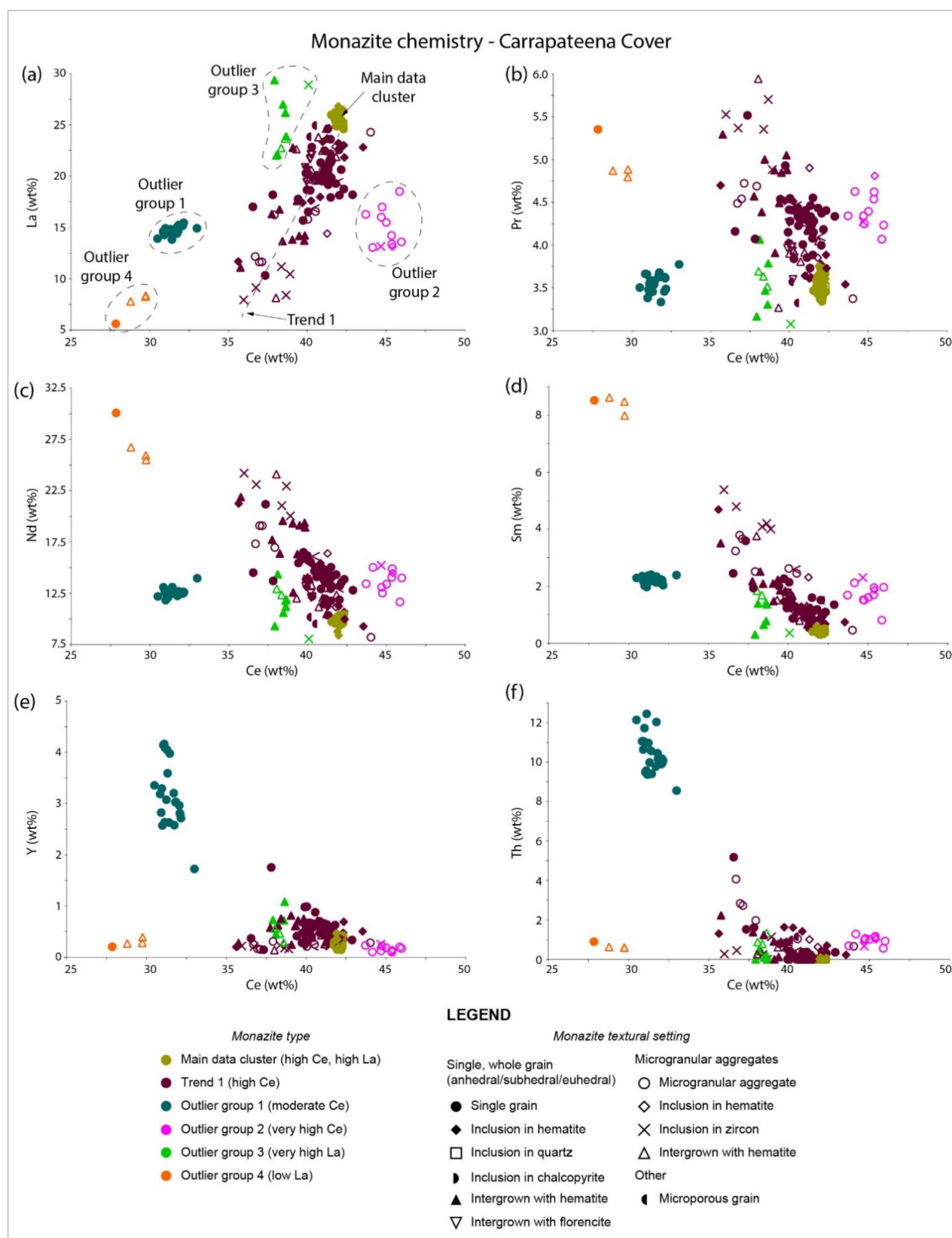


Figure 7. Geochemical plots for monazite from the cover sequence overlying the Carrapateena deposit. (a) Ce vs. La; (b) Ce vs. Pr; (c) Ce vs. Nd; (d) Ce vs. Sm; (e) Ce vs. Y; and (f) Ce vs. Th.

Table 2. Chemistry of selected elements of monazite grains from Carrapateena basement and overlying basal cover sequence diamictite. Patterns of ratios of La/Ce, (La + Ce)/Y, (La + Ce)/Th and (La + Ce)/Nd are highlighted in dark grey. Details on monazite grain type and location within the diamictite are given.

	n	La	Ce	La/Ce		Y	Th	(La+Ce)/Y		(La+Ce)/Th		Pr	Nd	Sm		(La+Ce)/Nd		Monazite Grain Types	Location Within Diamictite
Basement Monazite—Carrapateena																			
Group 1	37	23.2–27.5	41–42.5	0.55–0.65	High	0.1–0.5	up to ~0.2	126–558	Mod-High	312–5 M	Mod-High	3.1–3.9	8.3–11.1	0.1–0.8	5.9–8.4	High		whole grains (15); inclusions within hematite (19)	
Group 2	44	9.1–21.7	36.2–42.2	0.25–0.53	Low-Mod	0.1–0.7	up to 1.1	93–775	Mod-High	52–4 M	Mod-High	3.9–5.5	13.2–24.4	1.1–4.8	1.9–4.7	Low-Mod		inclusions within hematite (25); whole grains (6)	
Group 3	2	~15.5	~32.6	0.47–0.48	Mod	~3.1	~9.0	15–16	Low	5.3–5.4	Low	~3.5	~12.8	~2.2	~3.8	Mod		whole grains (2)	
Cover Sequence Monazite																			
Main data cluster	37	24.6–26.8	41.5–42.3	0.58–0.64	High	0.1–0.5	up to ~1	145–463	Mod-High	747–5 M	Mod-High	3.3–3.8	8.4–10.4	0.3–0.6	6.4–8.2	High		whole grains (20); inclusion within hematite (13) or quartz (4)	hematite-rich clasts (35); volcanic clasts (2)
Trend 1	104	7.9–25.0	35.6–44.0	0.21–0.62	Mod-High	0.1–1.8	up to ~5.2	32–340	Low-High	10–4.8 M	Low-High	3.3–6.0	8.2–24.2	0.5–5.4	1.8–8.3	Low-High		whole grains (47); microgranular aggregates (7); inclusions within hematite (14) or zircon (5); intergrown with hematite (22) or florencite (6)	hematite-rich clasts (72); granite clasts (5); volcanic clasts (3); chlorite±sericite altered granite clasts (5); quartz grain (2); matrix (17)
Outlier Group 1: moderate Ce	23	13.8–15.5	30.5–33.0	0.44–0.48	Mod	1.7–4.1	8.6–12.5	11–28	Low	3.7–5.6	Low	3.3–3.8	11.8–14.0	2.0–2.4	3.4–3.9	Mod		whole grains (23)	granite clasts (18); quartz grain (3); chlorite-altered granite clasts (2)
Outlier Group 2: very high Ce	11	13.1–18.5	43.7–46.0	0.29–0.40	Low-Mod	0.1–0.3	0.56–1.28	225–558	High	45–116	Mod	4.1–4.8	11.7–15.2	0.8–2.3	3.8–5.2	Mod		microgranular aggregate (9); inclusions within zircon (1) or hematite (1)	chlorite-altered granite clast (7); hematite-rich clast (3); granite clast (1)
Outlier Group 3: very high La	9	22.0–29.4	37.9–40.1	0.59–0.77	High	0.3–1.1	up to ~1.3	58–217	Low-Mod	47–4.7 M	Mod-High	3.1–4.1	8.1–14.4	0.3–1.8	4.2–8.6	Mod-High		intergrown with hematite (8); inclusion within zircon (1)	hematite-rich clast (8); granite clast (1)
Outlier Group 4: low La and Ce	4	5.6–8.4	27.9–29.8	0.20–0.28	Low	0.2–0.4	0.59–0.90	97–161	Mod	37–65	Mod	4.8–5.4	25.5–30.1	8.0–8.6	1.1–1.5	Low		microgranular aggregate in hematite (3); whole grain (1)	hematite-rich clast (4)

Monazite grains within basement rocks are split into three groups (Figure 6). The first group (Group 1: $n = 37$) preserves high La/Ce and (La + Ce)/Nd and moderate (La + Ce)/Y and (La + Ce)/Th. Data are taken from monazite grains that mostly occur as whole grains ($n = 15$) or as inclusions within hematite ($n = 19$). Three spots are from monazite inclusions within chalcopyrite. The second group (Group 2: $n = 44$) preserves low-moderate La/Ce and (La + Ce)/Nd and low (La + Ce)/Y and (La + Ce)/Th. The monazite grains are mostly inclusions within hematite ($n = 25$) with lesser as whole grains ($n = 6$). Thirteen spots are from microgranular aggregates of monazite, nine of which are also inclusions within hematite. The third group (Group 3: $n = 2$) preserves moderate La/Ce and (La + Ce)/Nd and low (La + Ce)/Y and (La + Ce)/Th. Both data are from whole monazite grains.

The REE, Y and Th concentrations of monazite in the cover sequence are variable (Figure 7). A tight cluster of data ($n = 37$) is characterised by high La/Ce and (La + Ce)/Nd and moderate (La + Ce)/Y and (La + Ce)/Th. All these data are from monazite within hematite clasts except for two, which are preserved within volcanic clasts. The monazite grains are mostly whole ($n = 20$) or occur as inclusions within hematite grains ($n = 13$). Four analyses are from monazite inclusions within quartz.

The largest group of data ($n = 104$) forms a trend ('Trend 1' in Figure 7; Table 2). Trend 1 shows high La/Ce and (La + Ce)/Nd and moderate-high (La + Ce)/Y and (La + Ce)/Th. Data following this trend are mostly derived from hematite-rich clasts ($n = 72$), with lesser from the matrix ($n = 17$), granite ($n = 5$), volcanic clasts ($n = 3$), chlorite $\pm$ sericite altered granite clasts ($n = 5$) and quartz grains ($n = 2$). The monazite grains themselves occur in a variety of textures, including as whole grains or microgranular aggregates, as inclusions within hematite or zircon or intergrown with hematite or florencite (Figure 5).

Four outlier groups are identified (Figure 7; Table 2). Outlier Group 1 ($n = 23$) follows moderate La/Ce and (La + Ce)/Nd and low (La + Ce)/Y and (La + Ce)/Th. Data defining this trend are all sourced from whole grains that are preserved within granite clasts ($n = 18$), quartz grains ($n = 3$) and chlorite-altered granite clasts ($n = 2$). Outlier Group 2 ($n = 11$) is characterised by very high Ce (~43.7–46.0 wt%). These monazite preserve low-moderate La/Ce, moderate (La + Ce)/Nd, high (La + Ce)/Y and moderate (La + Ce)/Th. Monazite is preserved within chlorite-altered granite clasts ($n = 7$), hematite-rich clasts ($n = 3$) and granite ($n = 1$). Nine of the analyses are from whole grains within microgranular aggregations; one is from an aggregation within a zircon and one is an aggregate within a hematite grain. Outlier Group 3 ($n = 9$) preserves very high La (~20.0–29.4 wt%) relative to Ce (~37.9–38.7 wt% with one analysis preserving 34.1 wt% Ce). These monazite preserve high La/Ce, moderate-high (La + Ce)/Nd, low-moderate (La + Ce)/Y and moderate-high (La + Ce)/Th. The data are from single grain inclusions in chalcopyrite and microgranular aggregates in hematite. Outlier Group 4 ($n = 4$) is characterised by low Ce (~27.9–29.8 wt%) and La (~5.6–8.4 wt%). The monazite therefore have low La/Ce and (La + Ce)/Nd ratios and also moderate (La + Ce)/Y and (La + Ce)/Th ratios. Three of these analyses are microgranular aggregate inclusions within hematite and one is a whole grain.

5. Discussion

5.1. Monazite in Carrapateena Basement Rocks

Separation of monazite from basement rocks at Carrapateena into three geochemical groups is controlled by light REE (LREE), middle REE (MREE), Y and Th content (Figure 6). The Y and Th content of Group 1 and Group 2 monazite are characteristically low (<1.1 wt%; Figure 6b,c); therefore, the L-MREE content is assessed here to understand the chemical distinction between the two groups. Comparison of the Ce + La content with MREEs Pr, Nd and Sm using traditional scatter plots shows a negative linear relationship (Figure 6d–f). This observation is compatible with substitution of middle REEs (MREEs) for LREEs in monazite at Carrapateena.

The two data that constitute Group 3 monazite in the Carrapateena basement rocks are distinguished by their high Y and Th content (Figure 6b,c). Processes involved in the

geochemical development of these monazite grains are considered separate from that of the Group 1 and 2 monazite and are considered below.

5.1.1. Comparison with Regional Background Chemistry

Ref. [3] considered that the chemistry of monazite from the broader Gawler Craton is representative of background monazite chemistry. The background samples include metamorphic monazite, monazite hosted within shear zones and monazite from the Challenger Au deposit (Figure 8). Comparison of monazite derived from mineralised basement rocks in the Carrapateena deposit with background monazite chemistry highlights the characteristically high Ce and La content of Group 1 monazite, the high Ce content of Group 2 monazite and the low Y and Th content of both Group 1 and Group 2 monazite. Ternary plots and scatter plots of corresponding ILR variables are used to understand the distribution of sample compositions (see Figures 8 and 9, which show the distribution of samples for Ce, La, Y and Th in the Carrapateena basement and background data). Three compositional groups of Carrapateena basement data can be distinguished, confirming the results indicated in the element scatter plots, i.e., that Group 1 and 2 Carrapateena monazite have a distinct chemistry relative to background monazite compositions.

Conversely, the chemistry of Group 3 Carrapateena monazite overlaps with the background data, which includes most metamorphic monazite and monazite from the Karari and Yerda shear zones (Figures 8 and 9). The majority of the Coorabie and Kalinjala shear zone and the Challenger deposit data and a minor portion of the Karari and Yerda shear zone data is spread along the ILR Y_LaCe axis and to a lesser extent the ILR Th_LaCe axis (Figure 9b,c,e,f), indicating a process of exchange between Y (and possibly Th) and LREEs.

The geochemical variations between Group 1 and 2 and Group 3 and background monazite indicates different processes influenced the monazite composition. The low Th content of the Group 1 and 2 monazite (<~1 wt%) is indicative of hydrothermal monazite [37] and the LREE-enriched nature of Group 1 and 2 monazite indicates La and Ce are the dominant elements being incorporated into the crystal lattice. Hydrothermal fluids associated with generation of IOCG systems in the Olympic Domain of the Gawler Craton have been determined to have been REE enriched [22,38]. The F- and CO₂-rich nature of the hydrothermal fluids promoted REE mobility [38]. Therefore, the Group 1 and 2 Carrapateena monazite are interpreted here to be linked with growth in association with LREE-enriched hydrothermal fluids associated with IOCG mineralisation and that La and Ce were concentrated in the monazite due to the predilection of monazite for LREEs [39,40].

In contrast, the high Th content of Group 3 and background monazite indicates monazite growth (and resorption) via processes other than in association with hydrothermal activity. Such processes may include metamorphism, partial melting and migmatization [3,41–44]. The lack of trends connecting chemical compositions of the Group 1 and 2 Carrapateena monazite with Group 3 Carrapateena and background monazite in ILR space (Figure 9) supports the interpretation that different processes influenced the monazite composition.

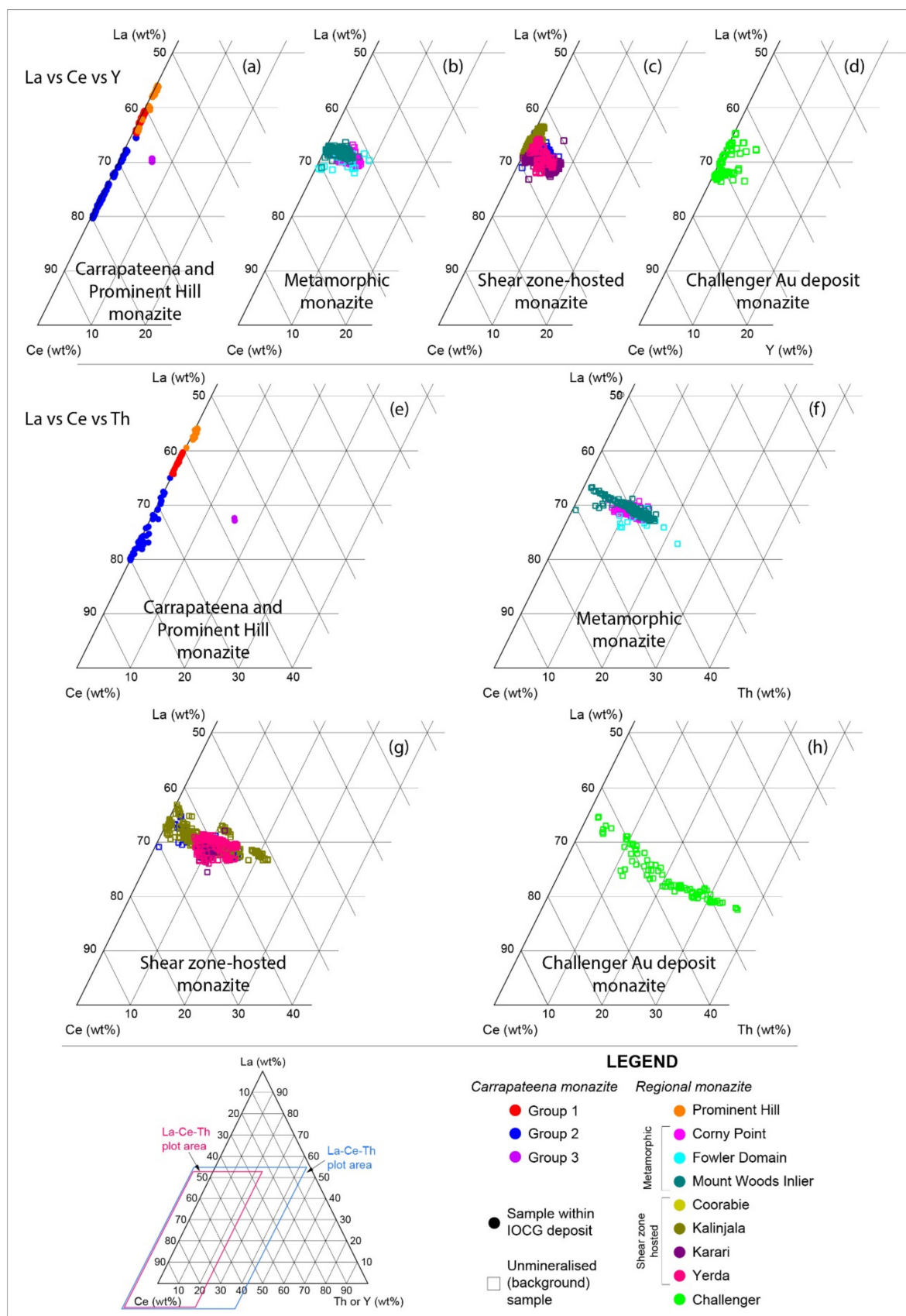


Figure 8. Ternary La vs. Ce vs. Y (a–d) and La vs. Ce vs. Th (e,f) diagrams for basement monazite from the Carrapateena and Prominent Hill deposits (a,e) and unmineralized basement including metamorphic monazite (b,f), shear zone-hosted monazite (c,g) and monazite from the Challenger Au deposit (d,h).

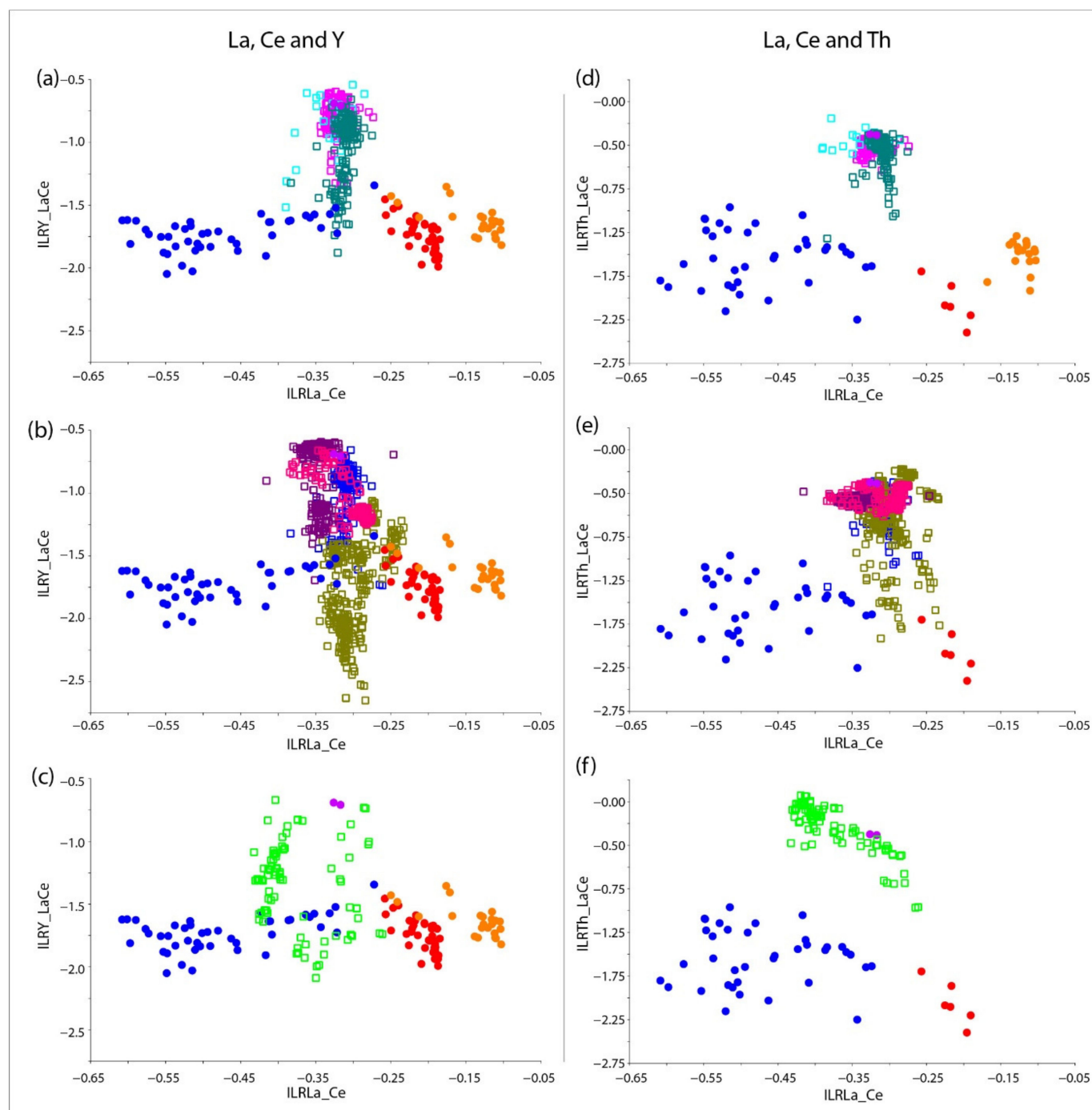


Figure 9. Isometric log ratio plots comparing La, Ce and Y (a–c) and La, Ce and Th (d–f) contents for metamorphic (a,d); shear zone hosted (b,e) and Challenger Au (c,f) monazite. Legend given in Figure 7.

5.1.2. Carrapateena Monazite Geochemical Criteria

The unusual composition of the hydrothermal monazite at Carrapateena (Group 1 and 2 monazite) can be used to develop an exploration tool that distinguishes background from anomalous data. Following [3], Ce vs. La, La + Ce vs. Y and La + Ce vs. Th diagrams are used due to the ability to separate the background from Group 1 and 2 Carrapateena monazite data on these diagrams. Additionally, the Nd content of Carrapateena monazite is identified as a distinguishing feature.

In the Ce vs. La diagram, Group 1 Carrapateena monazite define a composition of interest where Ce is >41 wt% and La is >22.5 wt% (Figure 6a). In the La + Ce vs. Y, La + Ce vs. Th and La + Ce vs. Nd diagrams, two compositions of interest are identified. The first composition is defined by Group 1 Carrapateena monazite that preserves La + Ce > 65 wt%, Y or Th < ~1 wt% and Nd < 12.5 wt% (Figure 6b,c). The second composition is defined by Group 2 Carrapateena monazite and can be identified by 45 wt% < Ce + La < 63 wt%, Y or Th < ~1 wt% and Nd > 12.5 wt% (Figure 6b,c,e).

5.2. Monazite in Carrapateena Cover Rocks

Several monazite grains preserved within the cover sequence directly overlying the Carrapateena deposit preserve chemistry that is similar to or overlaps with the composition of Group 1 and 2 monazite grains from the Carrapateena basement rocks (Figure 10), and that is demonstrably different from the background chemistry of monazite from elsewhere in the Gawler Craton.

Several cover sequence grains ($n = 48$) preserve elevated LREE content (Ce > 41 wt% and La > 22.5 wt%). These grains also preserve depleted Y and Th and low Nd compositions (Ce + La > 65 wt%; Y and Th < ~1 wt% and Nd < 12.5 wt%) and therefore have a chemistry that overlaps with the composition of the Group 1 basement monazite grains. The cover sequence monazite with chemistry like Group 1 are primarily located within hematite-rich clasts and are mostly whole grains or inclusions within hematite (Figure 10; Table 3). A significant number of monazite grains ($n = 109$) preserve LREE chemistry of 45 wt% < La + Ce < 65 wt%. Most of these grains ($n = 71$) also contain Y and Th < 1 wt% and Nd > 12.5 wt% and therefore preserve a composition that overlaps with the Group 2 basement monazite grains. These cover sequence grains are mostly located within hematite-rich clasts and are whole grains or intergrown with hematite (Figure 10; Table 3).

Table 3. Comparison of chemistry for Group 1 and Group 2 basement monazite chemistry with chemistry of monazite from cover sequence immediately overlying the Carrapateena deposit. Detail on the texture and location of monazite within the cover sequence is also given.

Carrapateena Basement			Carrapateena Cover		
Monazite Group	Monazite Chemistry	#Grains with Overlapping Chemistry	Monazite Type (see Figure 6 and Table 2)	Monazite Texture (#Grains)	Monazite Location Within Diamictite (#Grains)
Group 1	Ce > 41 wt%; La > 22.5 wt%; Ce + La > 65 wt%; Y and Th < 1 wt%; Nd < 12.5 wt%	48	Main data cluster (high Ce and La, 37 grains); Trend 1 (high Ce, 11 grains)	Whole grains (WG) (23); WG inclusion within hematite (18); WG inclusion within quartz (4); microgranular aggregates (MGA) (1); MGA inclusion within hematite (1); MGA intergrown with hematite (1)	Hematite-rich clasts (43); volcanic clasts (2); chlorite-altered granite clast (2); matrix (1)
Group 2	45 wt% < La + Ce < 65 wt%; Y and Th < 1 wt%; Nd > 12.5 wt%	71	Trend 1 (high Ce, 64 grains); Outlier Group 2 (very high Ce, 4 grains); Outlier Group 3 (very high La, 2 grains)	Whole grains (WG) (38); WG intergrown with hematite (11); WG intergrown with florencite (4); WG inclusion within hematite (1); microgranular aggregate (MGA) (4); MGA intergrown with hematite (8); MGA inclusion in zircon (4); MGA inclusion in hematite (1)	Hematite-rich clasts (48); matrix (13); granite clasts (8); volcanic clasts (2)

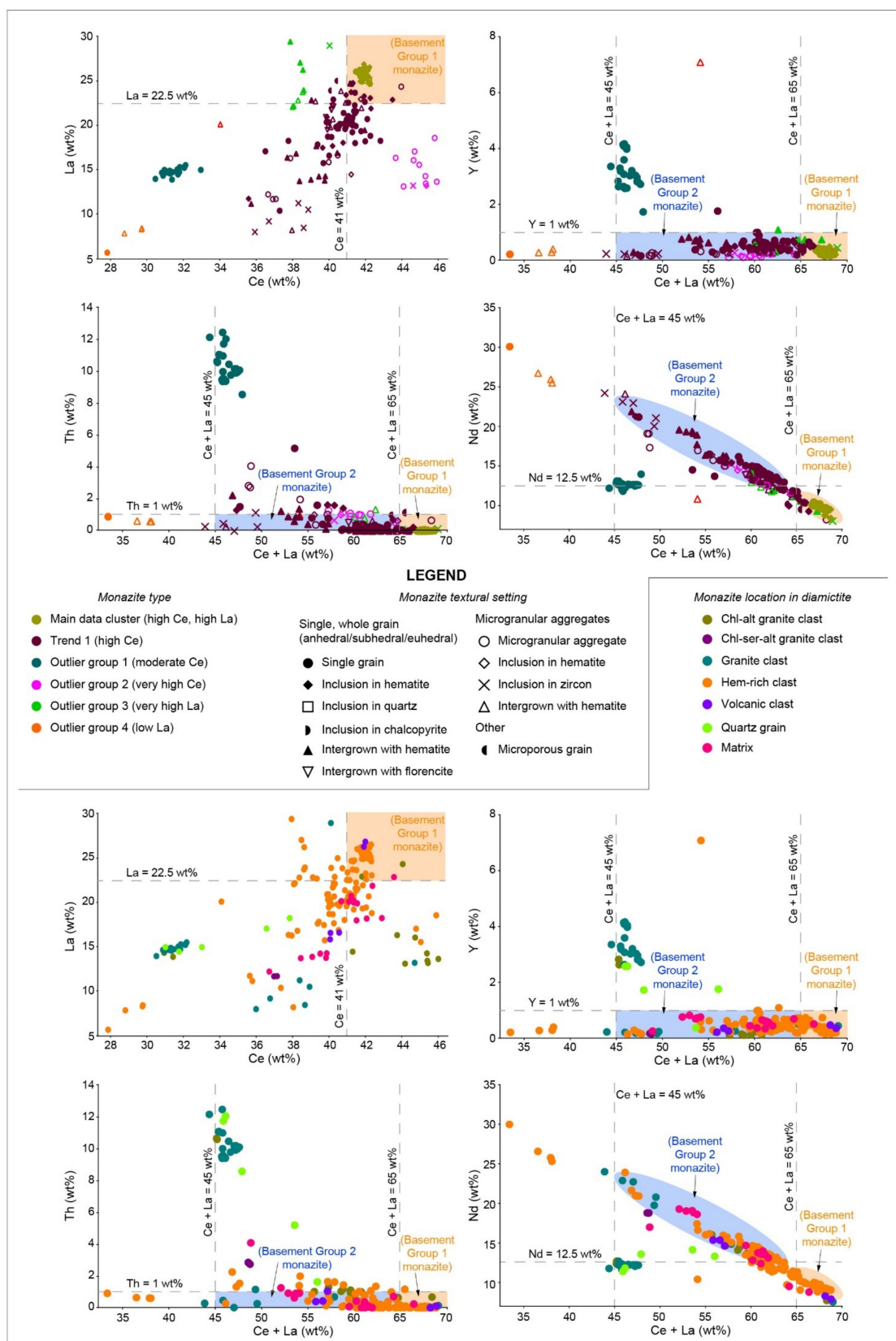


Figure 10. Plots of Ce vs. La and Ce + La vs. Y, Th and Nd for the Carrapateena cover sequence diamictite. Top set of plots is coloured by the monazite type (as per Figure 7) and shape depicts the monazite textural setting. Bottom set of plots is coloured by the location of the monazite within the cover sequence diamictite. The boundaries for Group 1 and Group 2 basement monazite Ce, La, Y, Th and Nd chemistry are shown.

The hematite-rich clasts that are the dominant host of the cover sequence monazite grains with chemistry overlapping with the Group 1 and 2 basement monazite are angular to subrounded in shape (Table 1), indicating no to minimal degree of transport prior to incorporation into the cover sequence. The combination of similar lithologies of the basement and cover sequence diamictite clasts, the angular to subrounded clast shape and the overlapping unusual LREE $\pm$ Nd-enriched, Y- and Th-depleted chemistry of the monazite in the mineralised basement and overlying cover rocks is used here to suggest that the clasts in the diamictite overlying the Carrapateena deposit were derived from the immediately underlying mineralised basement rock. These observations also suggest that monazite can withstand processes of weathering, erosion, transport and incorporation into cover sequence sedimentary materials. Similar conclusions were made by [3] in relation to Prominent Hill deposit monazite chemistry and incorporation into cover sequence materials. The preservation of monazite with interesting and compelling geochemical signatures that can be related to the underlying mineralised Carrapateena basement rocks also demonstrates the potential for the monazite geochemical signature to be dispersed within the cover sequence, effectively increasing the geochemical footprint of the mineral deposit.

Background monazite grains mostly occur within granite clasts ($n = 19$) with lesser in hematite-rich ($n = 6$) and chlorite-altered granite clasts ($n = 2$) as well as quartz grains ($n = 4$) (Figure 10). The more rounded nature of granite clasts (Table 1) indicates a degree of transport before incorporation into the cover sequence diamictite. Monazite preserving background geochemistry is interpreted to have been derived from outside of the Carrapateena deposit.

5.3. Regional IOCG Exploration Criteria

The geochemistry of monazite related to IOCG mineralisation has also been investigated by [3], who recognized that monazite within the Prominent Hill orebody preserves a unique LREE, Y and Th geochemical signature. Comparison of the monazite geochemical criteria for the Carrapateena deposit with the criteria developed by [3] for the Prominent Hill deposit (Figure 11a–c) allows the development of geochemical criteria across multiple deposits, thereby giving confidence in applying the criteria to IOCG exploration on a broader scale within the Gawler Craton (Figure 11d–f). Such exploration criteria for the Gawler Craton are significant as this region preserves the world's largest IOCG deposit, the Olympic Dam, and several additional economically significant deposits including Carrapateena and Prominent Hill. The Olympic Domain of the Gawler Craton is considered highly prospective for further discovery of major IOCG mineralisation [9].

Group 1 Carrapateena monazite has similar chemistry to the 'compelling' monazite from the Prominent Hill orebody. Group 1 Carrapateena monazite is more Ce-rich (>41 wt% relative to >37 wt% at Prominent Hill) (Figure 11a). Both Group 1 Carrapateena and Prominent Hill orebody monazite preserve similar La content (>22.5 wt%), low Y and Th content (<1 wt%) and low Nd content (<12.5 wt%) (Figure 6e,g; Figure 11a–c). Following the slightly lower Ce + La threshold of Forbes et al. (2015), which encompasses the Carrapateena Group 1 data, the criteria for compelling monazite chemistry for IOCG exploration in the Gawler Craton is herein defined as Ce + La > 63 wt%, Y and/or Th < 1 wt% and Nd < 12.5 wt% (Figure 11e,f).

'Interesting' monazite compositions at Prominent Hill are defined by 57.5 wt% $<$ La + Ce < 63 wt% [3]. Group 2 Carrapateena monazite compositions mostly overlap with the interesting Prominent Hill monazite chemistry; however, the range of Ce + La content for Carrapateena monazite is broader (45 – 65 wt%). Additionally, the Y or Th content for both Carrapateena and Prominent Hill monazite is consistently low (<1 wt%). The Nd content is elevated (>12.5 wt%) for the Carrapateena monazite; however, enrichment in MREE's was not observed in monazite derived from the Prominent Hill orebody (Figure 6e,g). These differences in monazite chemistry may be attributed to the composition of local hydrothermal fluids associated with IOCG mineralisation at Prominent Hill

versus Carrapateena, where Carrapateena was locally more enriched in MREEs, allowing for more extensive substitution of MREEs into the monazite crystal lattice. Combining the features of Group 2 and interesting monazite compositions from Carrapateena and Prominent Hill, respectively, interesting monazite compositions are herein defined by $45 \text{ wt}\% < \text{La} + \text{Ce} < 63 \text{ wt}\%$, Y and/or $\text{Th} < 1 \text{ wt}\%$ and possibly $\text{Nd} > 12.5 \text{ wt}\%$. Elevated MREE content is considered indicative of Carrapateena-style mineralisation rather than IOCG mineralisation in general.

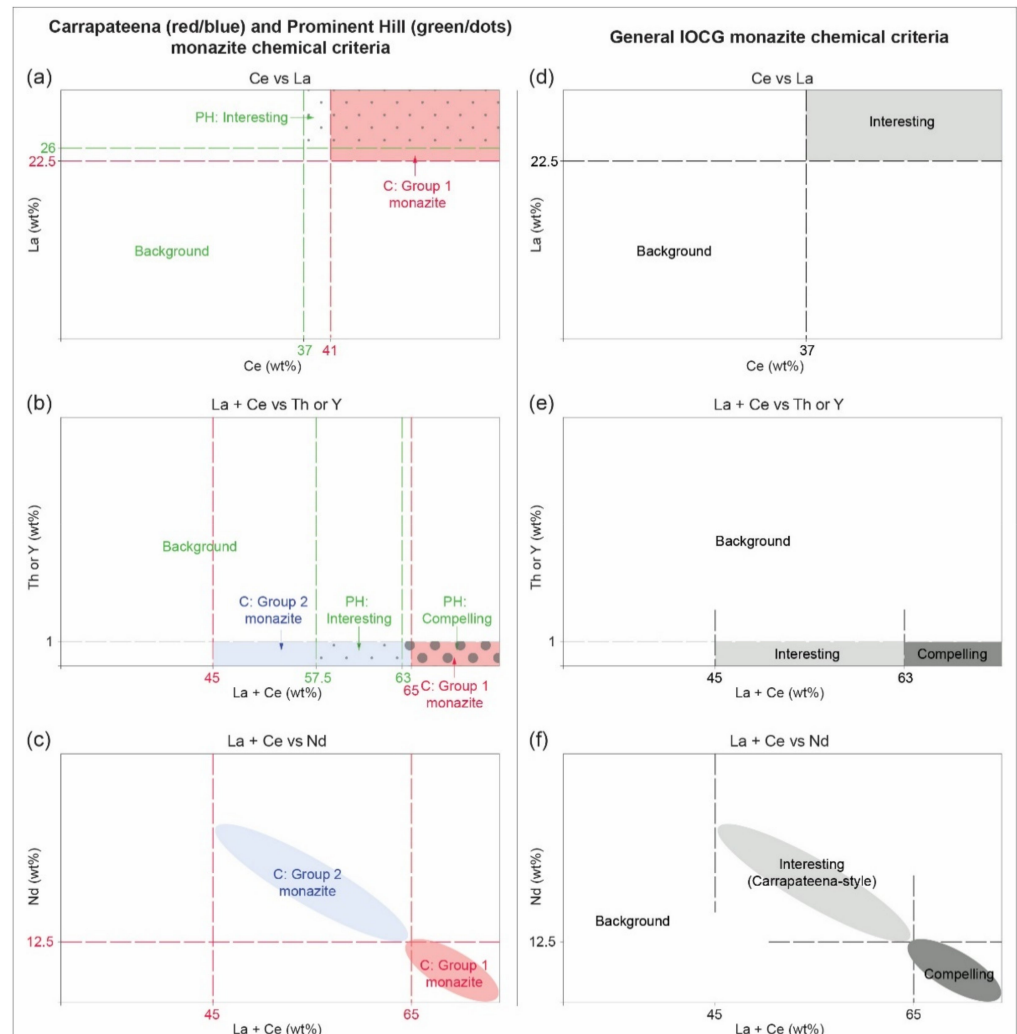


Figure 11. Monazite geochemical criteria for IOCG exploration. (a–c) Monazite geochemical criteria developed for Carrapateena (red/blue) and Prominent Hill (green/dots) using (a) Ce vs. La; (b) La + Ce vs. Th or Y; and (c) La + Ce vs. Nd. (d–f) Monazite geochemical criteria for IOCG exploration in the Gawler Craton using (d) Ce vs. La; (e) La + Ce vs. Th or Y; and (f) La + Ce vs. Nd. Monazite geochemical exploration criteria developed for the Prominent Hill IOCG deposit is taken from [3].

Background compositions are defined from the above criteria and using the composition of monazite grains sourced externally to IOCG mineralisation (i.e., metamorphic and shear zone hosted monazite). Background monazite compositions are therefore defined by $\text{La} + \text{Ce} < 45 \text{ wt}\%$ or Y or $\text{Th} > 1 \text{ wt}\%$.

The conclusion that clasts hosting monazite that preserves interesting to compelling chemistry in the cover sequence overlying the Carrapateena deposit derived from the underlying mineralized basement rocks is similar to observations made at Prominent Hill. Ref. [3] also concluded that interesting and compelling monazite preserved within clasts of

hematite breccia and skarn host within the glacial diamictite overlying the orebody were also derived from the underlying Prominent Hill mineralisation.

A suggested IOCG exploration sampling strategy for the Olympic Domain is therefore to target conglomerate and diamictite (and sedimentary breccia) cover sequence materials with a focus on hematite breccia, skarn and granite clasts. Ref. [3] demonstrated that sampling the cover sequence from 0–1 m above the basement–cover interface will give the best results. However, as noted by [3] and shown in this study, monazite grains with a chemistry reflective of monazite associated with IOCG mineralisation may also be preserved within cover sequence samples that are not located at the basement–cover interface.

6. Conclusions

The chemistry of hydrothermal monazite associated with IOCG mineralisation at Carrapateena and Prominent Hill in the Gawler Craton is recognised as having elevated LREE ($\text{La} > 22.5 \text{ wt\%}$; $\text{Ce} > 37 \text{ wt\%}$; $\text{La} + \text{Ce} > 63 \text{ wt\%}$), depleted Y and/or Th ($< 1 \text{ wt\%}$) and $\text{Nd} < 12.5 \text{ wt\%}$. Monazite compositions intermediate between background and ore-related monazite are considered interesting. Interesting monazite have a composition of $45 \text{ wt\%} < \text{La} + \text{Ce} < 63 \text{ wt\%}$, Y and/or Th $< 1 \text{ wt\%}$. Monazite indicative of Carrapateena-style mineralisation preserves $\text{Nd} > 12.5 \text{ wt\%}$. Background monazite compositions are defined as $\text{La} + \text{Ce} < 45 \text{ wt\%}$ or Y or Th $> 1 \text{ wt\%}$. Background compositions may indicate monazite of metamorphic origin or associated with shear zones.

Monazite with IOCG-related and interesting compositions is recognised within monazite host within basal cover sequence materials overlying IOCG mineralised basement rocks at Carrapateena. These observations have also been made at Prominent Hill (Forbes et al., 2015). The geochemical thresholds for monazite associated with IOCG mineralisation or considered here as interesting or background compositions are therefore used here to propose geochemical criteria for IOCG exploration in the Gawler Craton using monazite mineral chemistry. The geochemical signatures can survive processes of weathering, erosion, transport and redeposition into younger cover sequence materials that overlie the mineralised basement rocks, and therefore have the potential to be dispersed within the cover sequence, effectively increasing the geochemical footprint of mineralisation.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11080809/s1>, Table S1: Monazite mineral chemistry EPMA data for mineralised basement rock in the Carrapateena deposit and overlying basal conglomerate cover sequence samples.

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Appendix A

Full list of elements analysed (Table A1), primary and interference standards (Table A2) and detail of chemistry calculations.

Table A1. EPMA setup for spot analysis of monazite.

Element and Line	Diffracting Crystal (Sp#)	Background Type/Fit	kV/nA/Spot Size (µm)	Peak Count Time	Background Count Times		No. Background Points Acquired (Lo/Hi)	Standards *		Overlapping Element and Order/Interference Correction Standard							
					Lo	Hi		Primary Standard	Interference Standards	Interfering Line	Int. Std	Interfering Line	Int. Std	Interfering Line	Int. Std	Interfering Line	Int. Std
Ca Ka	LPET (1)	Shared	15/20/2	15	10	10	1/1	535									
U Mb	LPET (1)	Multipoint	15/100/2	40	20	20	1/2	631	629	Th Mg (I)	629						
La La	LPET (1)	Shared	15/100/2	30	15	15	0/4	1200	1201/1203	Ce La (I)	1201	Nd Lf	1203				
Ce La	LPET (1)	Shared	15/100/2	30	15	15	0/5	1201	1200	La Lb (I)	1200						
K Ka	LPET (1)	Shared	15/20/2	20	10	10	1/1	541	631	U Mb (I)	631						
Cl Ka	LPET (1)	Shared	15/20/2	20	10	10	1/1	545	1201/1203/1209/1210	Ce Lb (II)	1201	Nd La (II)	1203	Er Lb (III)	1209	Ho Lb (III)	1210
Na Ka	TAP (2)	Shared	15/20/2	15	10	10	1/1	501	631	U Ma (II)	631						
Si Ka	TAP (2)	Shared	15/20/2	20	10	10	1/1	501	1214	Y Ln (I)	1214						
Al Ka	TAP (2)	Shared	15/20/2	20	10	10	1/1	501	1209	Ho M2 (I)	1209						
Sr La	TAP (2)	Shared	15/100/2	30	15	15	1/3	513	631	U Mg (II)	631						
As La	TAP (2)	Shared	15/100/2	30	15	15	2/1	562	1203/1204/1207	Nd La (IV)	1203	Sm Mg (I)	1204	Tb Mb (I)	1207		
Fe Ka	LLIF (3)	Shared	15/20/2	30	15	15	5/0	502	629/1201/1205/1208	Th La (II)	629	Ce Lg (I)	1201	Eu Lb (I)	1205	Dy La (I)	1208
Gd Lb	LLIF (3)	Shared	15/100/2	30	15	15	1/1	1206	631	U La (II)	631						
Dy La	LLIF (3)	Shared	15/100/2	30	15	15	5/0	1208	629/1205	Th La (II)	629	Eu Lb (I)					
Tb La	LLIF (3)	Shared	15/100/2	30	15	15	5/0	1207	1202/1204	Pr Lg (I)	1202	Sm Lb (I)	1204				
Er La	LLIF (3)	Shared	15/100/2	30	15	15	1/1	1210	1207	Tb Lb (I)	1207						
Ho Lb	LLIF (3)	Shared	15/100/2	30	15	15	1/1	1209	631/1206	U La (II)	631	Gd Lb (I)	1206				
P Ka	LPET (4)	Shared	15/20/2	30	15	15	1/1	1201									
S Ka	LPET (4)	Shared	15/20/2	30	15	15	1/1	513	1200/1203	La La (II)	1200	Nd Lf (II)	1203				
Th Ma	LPET (4)	Shared	15/100/2	60	30	30	1/1	629	1206/1214	Gd La (II)	1206	Y Ka (V)	1214				
Y La	LPET (4)	Shared	15/100/2	500	25	25	1/1	1214	1200	La Lg (III)	1200						
Sm Lb	LLIF (5)	Shared	15/100/2	30	15	15	1/1	1204									
Eu La	LLIF (5)	Shared	15/100/2	30	15	15	1/1	1205	1202/1203	Pr Lb (I)	1202	Nd Lb (I)	1203				
Nd Lb	LLIF (5)	Shared	15/100/2	30	15	15	1/1	1203	631/1200/1201	U Lf (I)	631	La Lg (I)	1200	Ce Lb (I)	1201		
Pr Lb	LLIF (5)	Shared	15/100/2	30	15	15	4/0	1202	629/1200	Th Lf (II)	629	La Lb (I)	1200				

* Standard # refers to internal database. Full list of standards in Table 2.

Table A2. Primary and interference standard information.

Reference #	Mineral Composition	Natural/Synthetic	Manufacturer
501	Albite	Natural	Astimex
502	Almandine garnet	Natural	Astimex
504	Apatite	Natural	Astimex
513	Celestite	Synthetic	Astimex
535	Plagioclase	Natural	Astimex
541	Sanidine	Natural	Astimex
545	Tugtupite	Natural	Astimex
562	Gallium Arsenide	Synthetic	P&H and Associates
627	K227 (Pb silicate)	Synthetic	NIST
629	Huttonite	Natural	DAS
631	UO ₂	Synthetic	DAS
1200	LaPO ₄	Synthetic	Cherniak phosphate
1201	CePO ₄	Synthetic	Cherniak phosphate
1202	PrPO ₄	Synthetic	Cherniak phosphate
1203	NdPO ₄	Synthetic	Cherniak phosphate
1204	SmPO ₄	Synthetic	Cherniak phosphate
1205	EuPO ₄	Synthetic	Cherniak phosphate
1206	GdPO ₄	Synthetic	Cherniak phosphate
1207	TbPO ₄	Synthetic	Cherniak phosphate
1208	DyPO ₄	Synthetic	Cherniak phosphate
1209	HoPO ₄	Synthetic	Cherniak phosphate
1210	ErPO ₄	Synthetic	Cherniak phosphate
1214	YPO ₄	Synthetic	Cherniak phosphate

Detail of Chemistry Calculations

Oxygen was calculated by stoichiometry, assuming that all Fe was Fe²⁺. Matrix corrections of Armstrong-Love/Scott $\phi(\rho z)^2$ and Henke MACs were used for data reduction.

All elements were initially acquired using a traditional 2-point linear, excluding U Mb which was acquired using a multipoint fit. Following traditional 2-point background analysis, the ‘shared’ background fit option in Probe for EPMA was used across the list of elements. In simple background regions, a traditional 2-point linear fit was still used. For more complex regions of the spectrum, such as in the case some of the REE, multipoint or ‘shared’ fits were used to accurately model the background continuum and/or avoid off peak interferences.

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