



Rare earths and other trace elements in minerals from skarn assemblages, Hillside iron oxide–copper–gold deposit, Yorke Peninsula, South Australia

Roniza Ismail ^{a,b}, Cristiana L. Ciobanu ^{a,b,*}, Nigel J. Cook ^{a,b}, Graham S. Teale ^c, David Giles ^{a,b}, Andreas Schmidt Mumm ^{a,b,1}, Benjamin Wade ^d

^a Deep Exploration Technology Cooperative Research Centre (DET CRC), University of Adelaide, North Terrace, SA 5005, Australia

^b Centre of Tectonics, Resources and Exploration (TRaX), School of Earth and Environmental Sciences, University of Adelaide, North Terrace, SA 5005, Australia

^c Teale & Associates Pty Ltd., 82 Prospect Road, Prospect, SA 5082, Australia

^d Adelaide Microscopy, University of Adelaide, North Terrace, SA 5005, Australia

ARTICLE INFO

Article history:

Received 20 May 2013

Accepted 26 July 2013

Available online 2 August 2013

Keywords:

Iron oxide–copper–gold deposits

Skarn

Rare Earth Elements

Garnet

Titanite

Hillside

ABSTRACT

The Hillside Cu–(Au) deposit, Yorke Peninsula, South Australia, is a recently-discovered ore system within the 1.6 Ga World-class Olympic iron oxide–copper–gold (IOCG) Province. The deposit is characterized by a skarn-style alteration zone. Analyses of feldspar, calcite, skarn minerals (garnet, pyroxene, clinozoisite and actinolite) and accessories (titanite, apatite and allanite), and grain-scale element mapping by laser-ablation inductively-coupled plasma mass spectrometry are used to assess the distributions of rare earth element (REE), incompatible and ore-forming elements in host rocks, prograde and retrograde skarn.

Garnet is a major repository of HREE, especially in prograde skarn, whereas LREE-enriched clinozoisite is the principal REE-host in retrograde skarn. REE distribution patterns define a pronounced partitioning of elements among the dominant coexisting minerals. Compositional variation between assemblages, and also within individual grains, defines an evolution from early feldspar–pyroxene skarn through main-stage calcic skarn to the ore-stage. A switch from a prograde, HREE-dominant signature to a LREE-enriched signature is observed in both retrograde and distal skarn. Zr-in-titanite geothermometry supports transition from magmatic to hydrothermal, skarn-forming processes at temperatures of ~660 °C; the initiation of ore-stage is about 100 °C lower. Understanding REE distributions in all minerals within a complex, multistage ore system assists the development of vectoring tools that use trace element chemistry in exploration for similar IOCG deposits beneath regolith cover across the Olympic Province. Titanite and apatite show particular promise because of their characteristically distinct REE patterns in magmatic and hydrothermal stages, trace element responses to redox changes, and their widespread abundance throughout different lithologies in the area.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hypogene alteration in iron oxide–copper–gold (IOCG) systems is characterized in terms of a sequence of paragenetic mineral assemblages that result from fluid–rock interaction at scales ranging from regional to district to deposit. The Mesoproterozoic Olympic Province, South Australia, hosts a large number of World-class IOCG deposits (Skirow et al., 2007; Hayward and Skirow, 2010). Although host rocks vary, these deposits can be broadly divided into two types: giant sericite-altered, hematite-dominant IOCG systems (typified by Olympic Dam and Prominent Hill); and a group of deposits of comparable age in which both hematite and magnetite are present and which are associated with a marked skarn-like alteration signature that could represent a

deeper style of mineralization. Hillside, the subject of the present study, is within this latter group.

Since the bedrock of the Olympic Province has a negligible surface expression and lies under a thick cover sequence, there is considerable motivation to identify and understand the geochemical footprints of these ore systems and to develop vectoring tools that can be applied in exploration. Rare Earth Elements (REE) are abundant in most if not all IOCG systems (Hitzman, 2000; Williams et al., 2005), and although the elements are not extracted, the Olympic Province is one of the largest REE concentrations on Earth. The changing distribution of REE in a given mineral across the region is thus one potential guide to mineralization.

Research is focused on minerals which are ubiquitous in IOCG systems and their enclosing alteration envelopes, and which have been demonstrated to incorporate ppm-level concentrations of REE that can be quantified by analytical techniques such as laser-ablation inductively-coupled plasma mass spectroscopy (LA-ICP-MS). In order

* Corresponding author.

E-mail address: cristiana.ciobanu@adelaide.edu.au (C.L. Ciobanu).

¹ Present address: Saudi ARAMCO, 31311, Saudi Arabia.

to apply such tools, however, there is a need to understand REE distributions in all minerals within a given ore system, and the role which their partitioning among coexisting minerals plays during the lifespan of that system. Only then can the distribution patterns in selected minerals be considered as predictive tools for identification of proximal/distal or mineralized/non-mineralized relationships.

Similar approaches have been made to quantify REE deportment in granites (Bea, 1996; Gromet and Silver, 1983) but the work reported here represents the first attempt at building an integrated, holistic model of REE distribution in an IOCG-skarn system. We use changes in these elements within skarn minerals and accessories to monitor the evolution of alteration of the Hillside IOCG deposit, Yorke Peninsula, South Australia (Conor et al., 2010; Fig. 1). At Hillside, the alteration reflects a spatial-temporal development of ore zones rooted within

skarn alteration. The lead idea is that the trace element endowment in IOCG systems can be constrained and used for geochemical fingerprinting in a range of exploration templates. Results have general application to IOCG systems and could also be extended to other mineral systems assuming that geological processes involved can be constrained both spatially and temporally.

2. Background

2.1. The Olympic IOCG Province

The Olympic IOCG Province is the world's most richly-endowed IOCG ore province. It includes the super-giant Olympic Dam deposit, Prominent Hill, Carrapateena, Punt Hill, and other prospects (Hayward

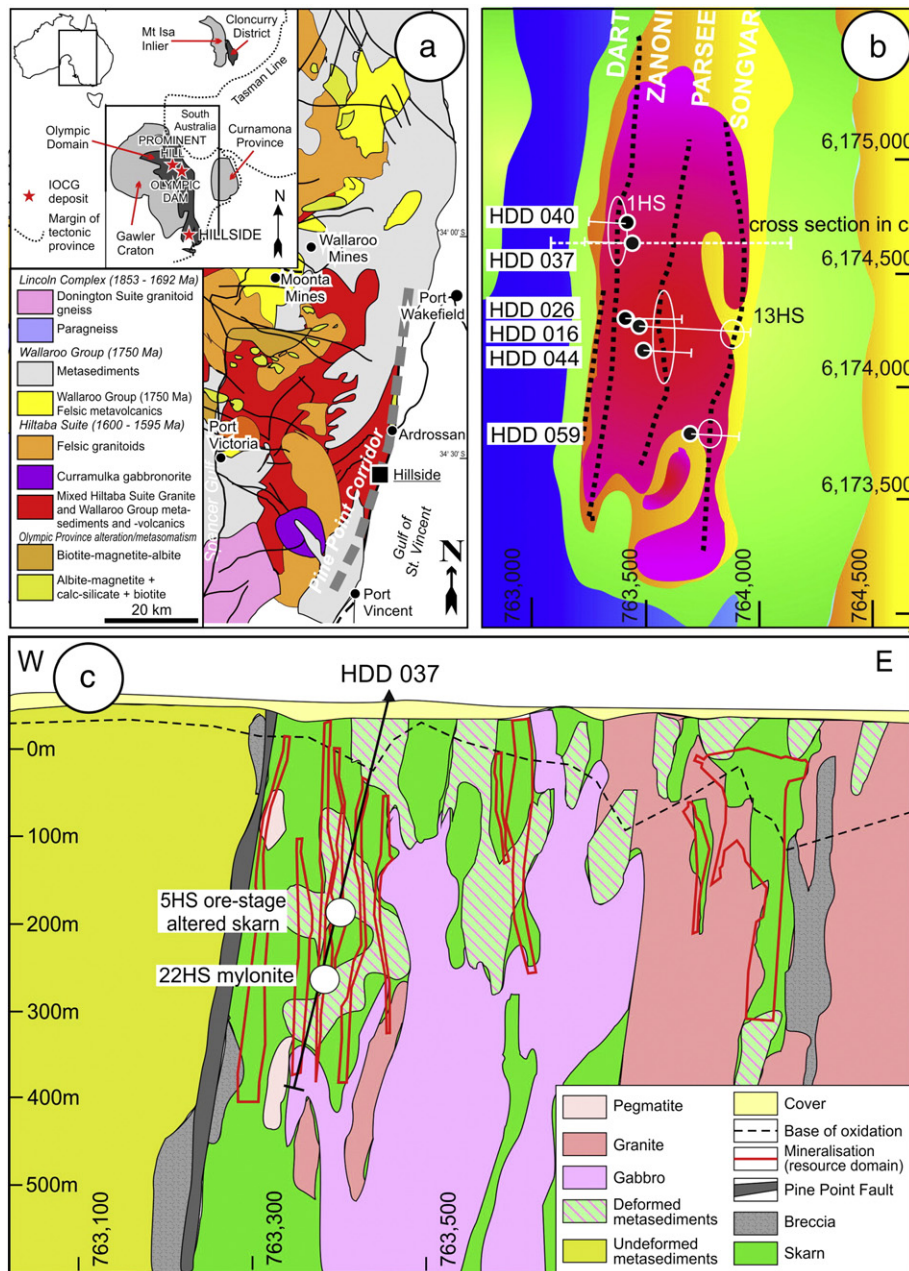


Fig. 1. (a) Geological sketch map of the northern part of the Yorke Peninsula showing Hillside and the Olympic Province. Inset shows the location of the Gawler Craton and other Australian IOCG-bearing provinces mentioned in the text (simplified after Conor et al., 2010). (b) Location of sampled drillholes projected onto the residual magnetic anomaly defining the Hillside deposit. Areas covered by sampling (Zanoni and Parsee orebodies) are circled. Locations of anomalously REY-rich sample (1HS) and sample 13HS from Songvaar are shown. (c) Schematic W–E cross-section (4600N transect, drillhole HDD037), showing typical position of skarn and orebodies relative to intrusives and host rocks. Panels (b) and (c) are simplified after company reports (www.rexminerals.com.au/).

and Skirrow, 2010). The province (Fig. 1a) is located along the eastern margin of the Gawler Craton, South Australia. Oxidized (magnetite-series), A- to I-type granitoid plutons of the 1595–1575 Ma Hiltaba Suite, and largely coeval intermediate to mafic volcanic rocks of the lower Gawler Range Volcanics (GRV), representing an intracontinental magmatic province (e.g., Hand et al., 2007), are emplaced within and erupted onto an accreted Palaeoproterozoic terrane (Hayward and Skirrow, 2010). Alteration and associated IOCG mineralisation formed between ~1570 and ~1600 Ma, temporally overlapping with magmatism (Hiltaba Suite and GRV) based on recent geochronological data for hydrothermal minerals (e.g., Skirrow et al., 2007; Ciobanu et al., 2013).

2.2. Deposit geology

The Hillside Cu–Au deposit was discovered in 2008 and inferred resources as of 30 July 2012 are 330 Mt at 0.6% Cu and 0.16 g/t Au, at a 0.2% Cu cut-off (Rex Minerals, 2012). The deposit is located within the N–S-striking Pine Point Fault Zone (PPFZ) which runs along the eastern coast of the Yorke Peninsula, South Australia (Fig. 1a). Mineralization is hosted by a highly-deformed sequence of metasedimentary rocks of the ~1750 Ma Moonta-Wallaroo (MW) Group, and Mesoproterozoic (1600–1575 Ma), Hiltaba Suite granites and gabbros (Conor et al., 2010). The deposit strikes N–S over a distance of ~2.5 km and is ~700 m wide. Four separate mineralized zones are recognized: Dart; Zanoni; Parsee; and Songvaar from W to E (Fig. 1b). All are coincident with a set of parallel faults within the PPFZ. These mineralized zones are concordant with the strike of the enclosing magnetic anomaly (Fig. 1b). Based on magnetic and gravimetric anomalies, gabbroic bodies are inferred to be present in extension of Hillside to both North and South, along the PPFZ, defining the Pine Point structural corridor. The western boundary of the deposit is considered as positioned between the undeformed (hanging wall) and deformed sediments of the MW Group.

Hypogene copper mineralization is dominated by chalcopyrite, which also hosts native gold. Mineralization has been confirmed from the base of the Cambrian to Tertiary cover sequence (5–30 m) to a depth of >700 m; the deposit is open at depth (Rex Minerals, 2012). The ore is hosted within steeply-dipping, sub-vertical, N–S-trending skarn and associated breccia bodies that vary in size both laterally and vertically (Conor et al., 2010). These bodies are placed either at the contact between highly-deformed sediments and magmatic rocks, or within the latter. Granite and gabbro appear interfingering with one another throughout the N–S strike of the deposit (Fig. 1c), even though the granite seems to be dominant on the eastern side.

The terms endo- and exoskarn are used by Conor et al. (2010) with reference to the alteration of gabbroic rocks. Although there is no mention of a precursor carbonate-bearing protolith accounting for exoskarn formation, the presence of such rocks can be postulated as interlayered sequences within the metasedimentary MW succession. Potassic alteration is reported either as an early, high-temperature or late, lower-temperature replacement of plagioclase in the gabbroic rocks by K-feldspar. Abundant pegmatites are emplaced along minor structures throughout the deposit; these may be intensively altered.

Skarn assemblages at Hillside include garnet, clinopyroxene, epidote-group minerals, actinolite, titanite, K-feldspar and associated magnetite. Conor et al. (2010) refer to garnet skarn (in some cases monomineralic) as higher-temperature relative to pyroxene skarn based on relationships between the two. Although pyrite and chalcopyrite formation is broadly attributed to the retrograde stage that overprints early, prograde skarn assemblages pyrite is also included in the higher temperature associations.

Gregory et al. (2011) constrain the age of skarn mineralization at Hillside by SHRIMP U–Pb dating of titanite and allanite at 1601 ± 16 Ma to 1584 ± 7 Ma. SHRIMP U–Pb zircon dating of altered granites give ages of 1602 ± 13 Ma and 1588 ± 10 Ma.

The structural style of the mineralization at Hillside has been compared to that at Moonta-Wallaroo, 60 km to the north-west, some IOCG-style deposits in the Curnamona Province, Eastern South Australia, and to the deeper Cloncurry-style IOCG-(U) deposits, Queensland (Conor et al., 2010). It is thus markedly different to the hematite-dominant, breccia-hosted Olympic Dam deposit. The deposit nevertheless possesses common features of IOCG-(U) deposits in the Gawler Craton: (1) ages of mineralization and alteration are coeval with Hiltaba Suite magmatism; (2) replacement of magnetite by hematite accompanied copper mineralization; (3) proximity to a major magnetic-gravity structure; and (4) strong structural control on mineralization.

3. Lithologies

Lithological recognition of hand-specimens at Hillside is often difficult on account of the broad similarity of mineral associations and coloring in host rocks, skarns, and in some cases, also the altered intrusive units.

Host rocks include a variety of banded lithologies. Those characterized by pink/red-and-green colors (Fig. 2a), are easily attributable to the MW Group. Feldspars form the pink/red bands whereas various assemblages of epidote and/or actinolite and chlorite occur in the green bands. Feldspars and Fe-oxides are also present in 'red-rocks' (Fig. 2b), which have a banded, BIF-like appearance, or in quartzitic mylonites (Fig. 2c). Sequences of impure carbonates and fine-grained chlorite schists, sometimes with abundant pyrite and minor Fe-oxides, are also part of the MW Group. Overall, the host rocks are mildly to intensely deformed, and are crosscut by sets of quartz and/or carbonate veinlets.

The main types of *igneous rocks* are gabbros and rocks from the granite family; they both span a range of grain sizes. Although gabbros are usually coarse-grained, with a salt-and-pepper-like appearance (Fig. 2d), they can be difficult to recognize when intensively altered to chlorite. Finer-grained mafic rocks are also present, either as marginal facies of intrusive apophyses, interstratified within other lithologies, or as crosscutting dikes. Granitic rocks are typically less altered than gabbro, although mafic minerals within them can display advanced chloritization and sericitization. Granites may also have a salt-and-pepper-like appearance (Fig. 2e), but finer-grained varieties can be difficult to distinguish from feldspathic MW rocks or skarns. Cross-cutting granite pegmatites (Fig. 2f) are common, and can display intense deformation.

Skarns are heterogeneous on the decimeter-scale and have similar colors as the MW rocks or some igneous rocks. They are commonly fine-grained even though coarser varieties, in particular garnetites, are also present. In the latter, variation in color and textures is observed, e.g., grains up to several cm-size display massive brown cores with comparably-sized margins showing oscillatory zoning with coloring from light-brown to dark green. Skarns almost always contain some feldspar (Fig. 2g, h). Epidote skarns may contain mm-to cm-size allanite (Fig. 2h). Decimeter-sized pods of coarser, or even pegmatitic allanite (up to 6–7 cm in diameter), can be present. The latter allanite clearly crosscuts boundaries between magnetite and quartz and/or calcite. Although late-stage, such grains are further fractured and in-filled by quartz and/or calcite (Fig. 2i). The relict character of the feldspar is shown by scalloped margins and enclosing, dm-scale halos of green skarn minerals (Fig. 2j). Although monomineralic garnet skarn is observed, garnet more commonly occurs together with pyroxene and epidote-group minerals (Fig. 2k).

Magnetite and less hematite are abundant in most skarns; textures ranging from disseminated to more massive (Fig. 2l). Pyrite and chalcopyrite are widespread in skarn as disseminations, patches and small lenses. Disseminations, or cm-size patches or lenses of Cu–(Fe)–sulfides (bornite, chalcocite, and chalcopyrite), also occur within granite and gabbro. Rarely, coarse-grained (cm-size), pyrite forms dm-scale intervals (Fig. 2m). Bands of massive chalcopyrite, 10–20 cm in thickness (Fig. 2n) characterize high-grade intersections but ore typically consists

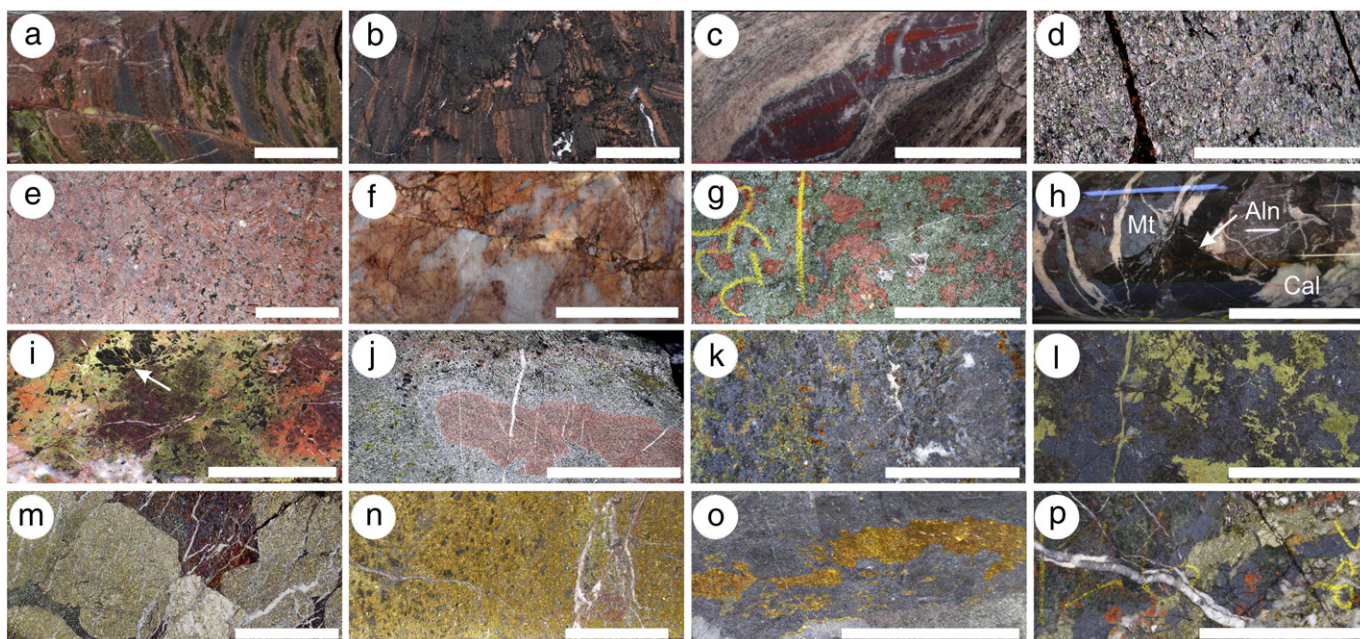


Fig. 2. Photographs of hand-specimens of typical lithologies. (a–c) Banded, 'red-rock' and mylonite lithologies, Moonta Wallaroo Group. (d, e) 'Salt-and pepper'-like appearance of coarse-grained gabbro and granite. (f) Granite pegmatite. (g) Skarn with green pyroxene matrix and pink feldspar enclaves. (h) Skarn containing cm-sized allanite (Aln). (i) 'Pegmatitic' allanite crosscutting magnetite (Mt) and calcite (Cal). (j) Scalloped feldspar enclave enclosed in skarn. (k) Multi-component garnet-pyroxene-epidote skarn. (l) Magnetite-bearing skarn. (m) Intervals of coarse-grained pyrite. (n) Band of massive chalcopyrite (highest-grade ore). (o) Small-lenses of chalcopyrite in magnetite. (p) Late calcite-quartz veinlets crosscutting skarn assemblages. Scale-bars: 1 cm.

of small chalcopyrite lenses or veinlets (Fig. 2o). Late calcite-quartz veinlets crosscut all assemblages including sulfides (Fig. 2p).

4. Methodology

Petrographic-mineralogical study was carried out on ore-bearing samples from 6 drillholes intersecting the Parsee and Zanoni zones (Table 1; Fig. 1b), as well as a sample of relatively fresh granite. All skarns contain magnetite and hematite; variable amounts of pyrite and chalcopyrite are present in all except 3 samples. Determination of trace element concentrations and distribution in feldspars, main skarn minerals and accessories was undertaken on 20 samples, each prepared as a polished block (1-inch diameter). Although this sample suite is limited, it covers a 600 m-long N-S interval, includes skarn associations from two main ore zones and is thus considered representative. Routines for electron probe microanalysis (EPMA) and LA-ICP-MS are given as Electronic Appendix A.

5. Mineralogy and petrography

The presence of calc-silicates (epidote-group, actinolite) or magnetite in both skarn and rocks from the MW Group, or feldspars in skarns, MW and igneous rocks, renders recognition of the protolith for skarn formation difficult. It is likely that besides impure carbonate and gabbro already discussed elsewhere (e.g., [Conor et al., 2010](#)), several other rock types could have been protoliths, e.g., banded, calc-silicate-bearing, feldspathic rocks, feldspar-magnetite 'red-rocks' or granites. Other rocks, which display intense pyritization, such as chlorite schists, although not potential protoliths as such, may nevertheless include minerals of interest (apatite, minor pyroxene) since these are also present in skarn and provide a basis for comparison of REE trends.

End-member feldspars (K-feldspar and albite) are present in variable proportions throughout most skarns except in garnetites. The main skarn associations are calcic and comprise grandite-series garnets, pyroxenes from the hedenbergite-diopside series, clinozoisite and actinolite. Magnetite, always replaced by hematite to various degrees, is another ubiquitous component of the analyzed samples. Accessories

are abundant and include titanite, apatite and allanite; zircon is rarely observed. Calcite, quartz and chlorite are found in all skarn associations, either replacing pre-existing minerals or along veinlets.

EPMA data for key minerals in rock types listed in Table 1 are presented as Electronic Appendix B. There is no consistent variation in the major composition of garnet or pyroxene from North to South, or with depth (Fig. 3).

Garnet was analyzed in garnetite, as well as in the multi-component skarns. There is little variation in overall range of compositions (Electronic Appendix B1); most fall within a narrow compositional range ($\text{And}_{98}\text{Gr}_{2-}$ to $\text{And}_{75}\text{Gr}_{25}$; Fig. 3). An exception is seen in the oscillatory growth bands with clinozoisite where compositional variation ranges from $\text{And}_{100}\text{Gr}_0$ to $\text{And}_{48}\text{Gr}_{52}$ (e.g., 4HS).

Pyroxenes were analyzed in skarn (Electronic Appendix B2), and from inclusions in pyrite (sample 17HS attributed to MW Group). They range in composition from $\text{Di}_{71}\text{Hed}_{29}$ to $\text{Di}_{42}\text{Hed}_{57}$, encompassing both diopside and hedenbergite (Fig. 3); the latter is rarer. Pyroxenes contain <1 wt.% Al_2O_3 and, generally, negligible johannsenite component. EPMA data for actinolite (Electronic Appendix B2) show $\text{Mg}/(\text{Fe} + \text{Mg})$ ratios of ~0.75 and <0.5 wt.% Al_2O_3 .

EPMA data for epidote-group minerals (Electronic Appendix B3) typically shows 60–70 mol% clinozoisite and negligible piemontite content. Similar compositions are seen in coarse clinozoisite in sample 15HS (attributed to MW Group).

In skarn assemblages, plagioclase feldspar is represented solely by albite (< An_4). Potassium feldspar contains no more than 1–2 mol% $\text{NaAlSi}_3\text{O}_8$.

EPMA data for titanite (Electronic Appendix B4) shows little variation among hydrothermal titanite in different samples. The EPMA dataset for titanite in sample 7HS, employing an extended list of elements (Electronic Appendix B4), does, however, point to two sub-populations. The first, an early magmatic titanite (Ttn-1), contains higher ZrO_2 , Nb_2O_5 , REE_2O_3 than the second generation which has a composition comparable with that in other hydrothermal titanite. Ttn-1 and Ttn-2 do not differ in terms of Al and Fe content. Ttn-1 also contains detectable Cl (600 ppm).

Apatite (Electronic Appendix B6) contains a dominant fluorapatite component with negligible Cl and no calculated OH content; Fe, Si,

Table 1
Index of samples, locations and mineralogy.

Sample ID	Depth (m)	Rock type ^a	Main mineral association, key textures	Acc. minerals				Minor/trace minerals		
				Ap	Tit	Aln	Zrc	Other ore min.	Um	REEm
ZANONI										
4700N transect, drillhole HDD040- (138–152 m; high-grade intersection 14 m at 2.7% Cu, 0.6 g/t Au)										
HS1	150.5	Garnetite	Massive brecciated garnet-matrix to Mt–Py–Cp ore					Hm		
4600N transect, drillhole HDD037										
HS5	185.15	Ore-stage altered calcic skarn	Py–Cp–Hm in Qz + Cal + Chl matrix, relicts of skarn minerals; Aln as coarse grains; Kfs present	x		x		Mt, Gn		
HS22	256.1	Moonta Wallaroo (MW) mylonite	Fine-grained Qz–Chl schist with pronounced deformation	x				Mt, Hm, Py, Cp, Apy, Au	x	
PARSEE (except HS13 in SONGVAR)										
4300N transect, drillhole HDD016										
HS24	379.4	Feldspar–pyroxene skarn	KFs–Ab–Px and Mt; Tit–Px disequilibrium texture	xx	x			Hm, Cp		
HS25	387.9	Distal calcic skarn	Grt–Ep–Act with Mt–Py–Cp ore; relict Px and Ab present. Grt–Ep forms oscillatory growth bands	x				Hm		
HS3	389.5	Calcic skarn	Px–Ep skarn with Mt–Py ore; Act and relict KFs present	x	xx			Hm		x
HS13	542.7	Intensely-altered feldspar skarn	Mt–Hm in Cal–Qz, Chl matrix; abundant relict Kfs and Tit	x	xx			Cp		
4300N transect, drillhole HDD026										
HS12	363.2	Garnetite	Massive garnet-matrix to Mt–Py–Cp ore					Hm, Gn, Cas, (Bar)		
HS23	394.4	Ore-stage altered granite	Mt–Py–Cp ore in Qz–Carb–Chl matrix. Coarse KFs incipiently altered to Ep; abundant Aln as small grains	x		x		Hm		
4100N transect, drillhole HDD044										
HS15	126	MW (?) ‘green-rock’ I, skarn overprint	Coarse Ep–Qz–Cal rock with KFs, Grt, Px; ore minerals as dissem. & veinlets					Mt, Hm, Py, Cp, Gn, Hs		
HS7	148	Early feldspar–pyroxene skarn	Ab–Px–Mt; minor KFs present; Tit–Px disequilibrium texture. Coarse abundant Aln, Tit		xx	xx	x	Hm		x
HS16	155.2	Ore in hydrothermally altered rock	Hm–Py–Cp ore within Qz–Cal–Chl matrix	x	x			Gn, Au		
HS17	157	MW ‘green-rock’ II	Chl schist with Py–Mt; abundant Ap. Ap also with Px and KFs as inclusions in Py	xx	x			Hm, Cp, Gn		
HS18	163.6	Calcic skarn	Px–Act–Ep with Mt–Py–Cp ore; Kfs present. Pronounced retrograde overprint		x			Hm		
HS19	164	Distal skarn, marble contact	Mt–Py–Cp ore in coarse Cal; Grt present along crosscutting Cal-veinlets. Tit in Mt that is in-filled by Cp		x			Hm, <<Ilm, Gn		
HS8	170	Calcic skarn	Mt–Py–Cp ore as matrix to relict KFs containing Grt–Px–Ep–Act	x				Hm, Cas		
HS11	172.4	Calcic skarn	Mt–Py–Cp ore with Grt, KFs and Ab. Tit in Mt that is in-filled by Py		x			Hm, Gn	x	
HS6	175	MW ‘red-rock’	Coarse Kfs and Mt; Py, Cp present; incipient replacement of Kfs by Ep		x			Gn, trace Hm	x	
HS20	184	Ore in hydrothermally altered rock	Hm–Py–Cp ore within Qz–Cal–Chl matrix	x				Hm		
HS2	197	Ore in hydrothermally altered rock	Hm–Py–Cp ore within Qz–Cal–Chl matrix		x			Hm, Gn, Cas		
HS21	221	Garnetite	Massive garnet-matrix to Mt–Py–Cp ore		x			Hm		
HS10	233	Ore-stage altered calcic skarn	Mt–Py–Cp ore, minor Grt–Ep–Act–Kfs. Tit in Mt that is in-filled by Py		x			Hm, Gn–Cls, Gn		
HS4	273.5	Calcic skarn	Grt–Px–Ep with Mt–Py–Cp ore; Act and Ab present. Grt both zoned and unzoned, ring textures	x	x			Hm, Cc, Alt, Au, Gn, Cas		x
HS9	277.5	Ore in hydrothermally altered rock	Mt–Py–Cp ore in Qz–Cal–Chl matrix; minor Ab present	x				Hm		
3900N transect, drillhole HDD059										
HS14	100.45	Supergene alteration of Cu ore	Vuggy Qz–Chl matrix containing disseminated Cc					Mt, Hm, Cp		
Unknown drillhole										
HS26	–	Hillside granite	Alkaline granite (orthoclase, microcline) with hydrothermal alteration of mafic minerals	x			x	Ru, Ser, Chl, Mon		x

Abbreviations: Ab–albite, Act–actinolite, Aln–allanite, Alt–altaite, Ap–apatite, Apy–arsenopyrite, Au–native gold, Bar–baryte, Cal–calcite, Carb–carbonate, Cas–cassiterite, Cc–chalcocite, Chl–chlorite, Cp–chalcopyrite, Ep–epidote–clinozoisite, Gn–galena, Gn–Cls–galena–clausthalite solid solution, Grt–garnet, Hm–hematite, Hs–hessite, Ilm–ilmenite, Kfs–K-feldspar, Mon–monazite, Mt–magnetite, Px–pyroxene, Py–pyrite, Qz–quartz, Ru–rutile, Ser–sericite, Tit–titanite, Zrc–zircon, Um–uranium minerals, REEm–REE minerals.

All samples have minor Cal–Qz alteration, noted in table only when dominant. All calcic skarns contain some feldspars.

^a This terminology is used on all tables and diagrams.

Mg and Al are detected in most analyses. Data for *allanite* (Electronic Appendix B7) show Ce > La, negligible Y-content and Ca > 1 atom per formula unit in all analyses. Analyzed grains in sample 7HS are compositionally zoned with respect to Fe and Al; REE correlate positively with Fe.

EPMA data for *chlorite-group minerals* in 18 samples (Electronic Appendix B8) reveal a broad range of Mg/(Fe + Mg) ratios (0.25 to 0.66).

5.1. Moonta-Wallaroo host rocks

The MW 'red-rocks' (6HS) consist of coarse-grained K-feldspar with interstitial quartz and magnetite. The latter stands out against skarns in that it displays intense brittle fracturing but very little, if any, replacement by hematite. Coarse pyrite, which is also intensively fractured, occurs at contacts between magnetite and feldspar. Chalcopyrite is a

minor component, mostly in-filling fractures in pyrite. The sample includes titanite and apatite as well as incipient but pervasive replacement of K-feldspar by clinozoisite.

Clinozoisite-rich rocks (15HS) can be considered an equivalent of the 'green-rocks' within the MW Group (MW 'green-rock' I). This lithology is affected by metasomatism resulting in formation of garnet and pyroxene as well as deposition of Fe-oxides and sulfides within veinlets. This differs from skarn with similar composition in that there is a difference between coarse (mm-size) idiomorphic but intensely fractured, clinozoisite and the much smaller garnet or pyroxene.

Intensely *pyritized chlorite schists* (17HS) are another example of 'green-rocks' in the MW Group (MW 'green-rock' II). This lithology may include abundant, coarse apatite within a fine-grained chlorite matrix. Apatite, K-feldspar and calcic pyroxene all occur as small inclusions in pyrite. Whereas apatite in the matrix can be considered inherited

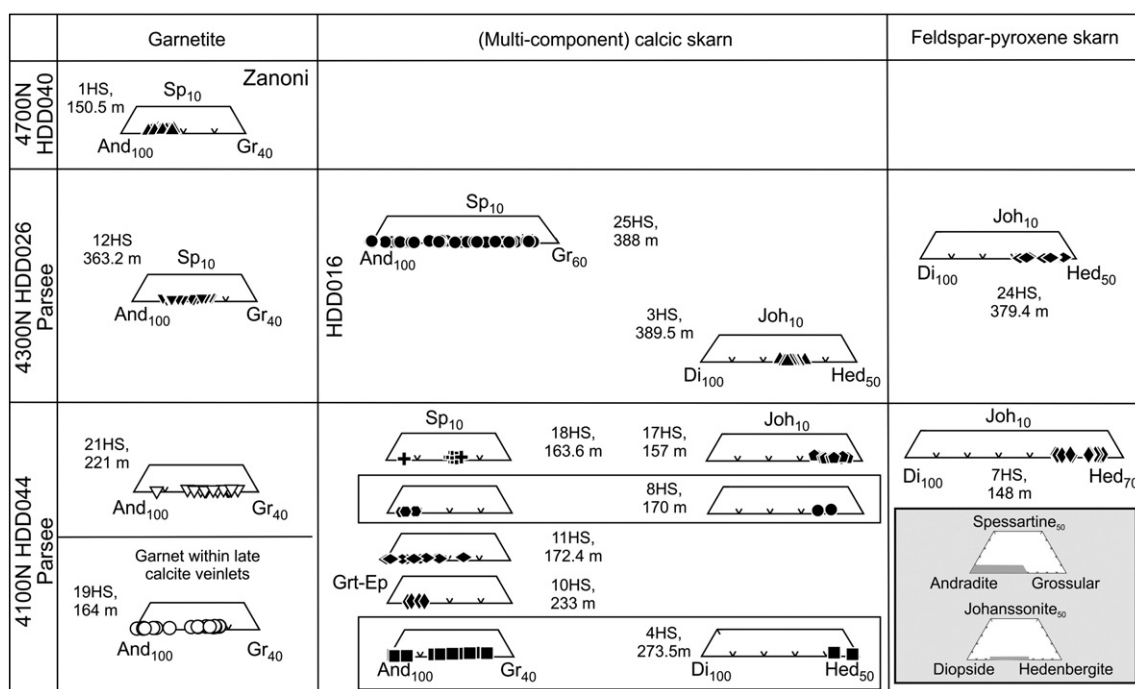


Fig. 3. Ternary diagrams (see inset, lower right) showing compositional variation in garnet and pyroxene (EPMA data) in different skarn types and parts of the deposit. See text for explanation.

from the protolith, the inclusions in pyrite can be tied to skarn formation. This rock, unlike other chlorite-rich schists or mylonites (e.g., 22HS), contains very little quartz, if any.

5.2. Hillside granite

The *granite* (26HS) contains two K-feldspars: coarse-grained orthoclase (~75%) and interstitial, finer-grained microcline (1–2%). Orthoclase features pervasive brittle fracturing. This leads to veinlets (widths from <1 to several hundred μm) characterized by porosity and sericitization, as well as by minute Fe-oxides, apatite and REE-minerals, including monazite. Domains containing lamellae with up to several hundred ppm Ba (brighter on BSE-images; Fig. 4a) are observed throughout the orthoclase. Orthoclase also shows slight foliation underlined by bundles of darker color containing relict biotite. They result from alteration of mafic minerals, and consist of fine-grained mixtures of sericite, chlorite and minor quartz along with abundant apatite and zircon (Fig. 4b); symplectites of rutile and chlorite locally form larger bundles. Zircon is fractured and displays compositional zoning that is dislocated and patchy in the core (Fig. 4c). Apatite preserves unaltered, zoned cores (magmatic origin) but the margins (hydrothermal) are fractured and outlined by monazite rims (Fig. 4d).

Ore-stage altered granite (23HS) is collected from the identical granite interval dated by Gregory et al. (2011). This is sulfide-rich, contains Fe-oxides, abundant allanite, titanite and apatite, and calcite-quartz veinlets. Relict K-feldspar occurs in a mixture of clinozoisite, calcite, quartz and chlorite.

5.3. Skarn assemblages

Based upon the relative proportions of feldspars and calc-silicates, as well as the single or multi-component associations of the latter, three main skarn types are defined: feldspar-pyroxene, garnetite and multi-component calcic skarns. Relationships between skarn minerals themselves are used to define prograde and retrograde stages.

5.3.1. Feldspar-pyroxene skarns

Albite and K-feldspar are the main components (~40–50%), in association with pyroxene (~35%), abundant accessory minerals and magnetite. The relative proportions and relationships between the two feldspars, and the type of accessories, are criteria for separating two sub-types: (i) albite-; and (ii) K-feldspar-dominated.

In the albite-dominant sub-type (7HS, Fig. 4e), K-feldspar is minor and patchy whereas in the K-feldspar-dominant sub-type (24HS), albite is coarse, with scalloped boundaries between the two feldspars. Both sub-types feature interstitial titanite between Fe-oxides, pyroxene and/or albite (Fig. 4f, g). The dominant type of titanite occurs as coarse, idiomorphic grains with internal zonation (Fig. 4h). In the albite-dominant type, abundant, compositionally-zoned allanite is characteristic (Fig. 4i) and also zircon. Characteristically, dusty to μm -sized Fe-oxides are observed as inclusions within both feldspars, outlining their mutual boundaries (Fig. 4j–l).

The two types of titanite (Ttn-1 and -2) in sample 7HS suggest inherited-magmatic and hydrothermal-overprint origins, respectively. Overall, the rock displays an oxidized character (absence of ilmenite, presence of hematite). In such rocks, titanite stability is governed by either bulk composition (rocks with high Ca/Al ratios such as metaluminous I-type granitoids), or crystallization conditions (mafic rocks where ulvöspinel is a component of magnetite and hedenbergite is a component of augite). The latter is ruled out since titanite and pyroxene are on opposing sides of stability-controlling mineral reactions and should not co-exist at equilibrium (e.g., Frost et al., 2000). The first alternative is consistent with the abundant allanite in the sample. Ttn-1 could result from late, syn- to post-magmatic re-equilibration in a typical calc-alkalic rock following a high-oxidizing ilmenite-dominant cooling trend (e.g., Frost et al., 2000). Ttn-2 is attributed to hydrothermal overprinting, as clearly shown by disequilibrium relationships with pyroxene (Fig. 4f, g).

Rock-types showing higher alteration (fine-grained mesh of calcite-quartz-chlorite but no skarn minerals) are included in this category (13HS) based on preserved contours of pre-existing minerals

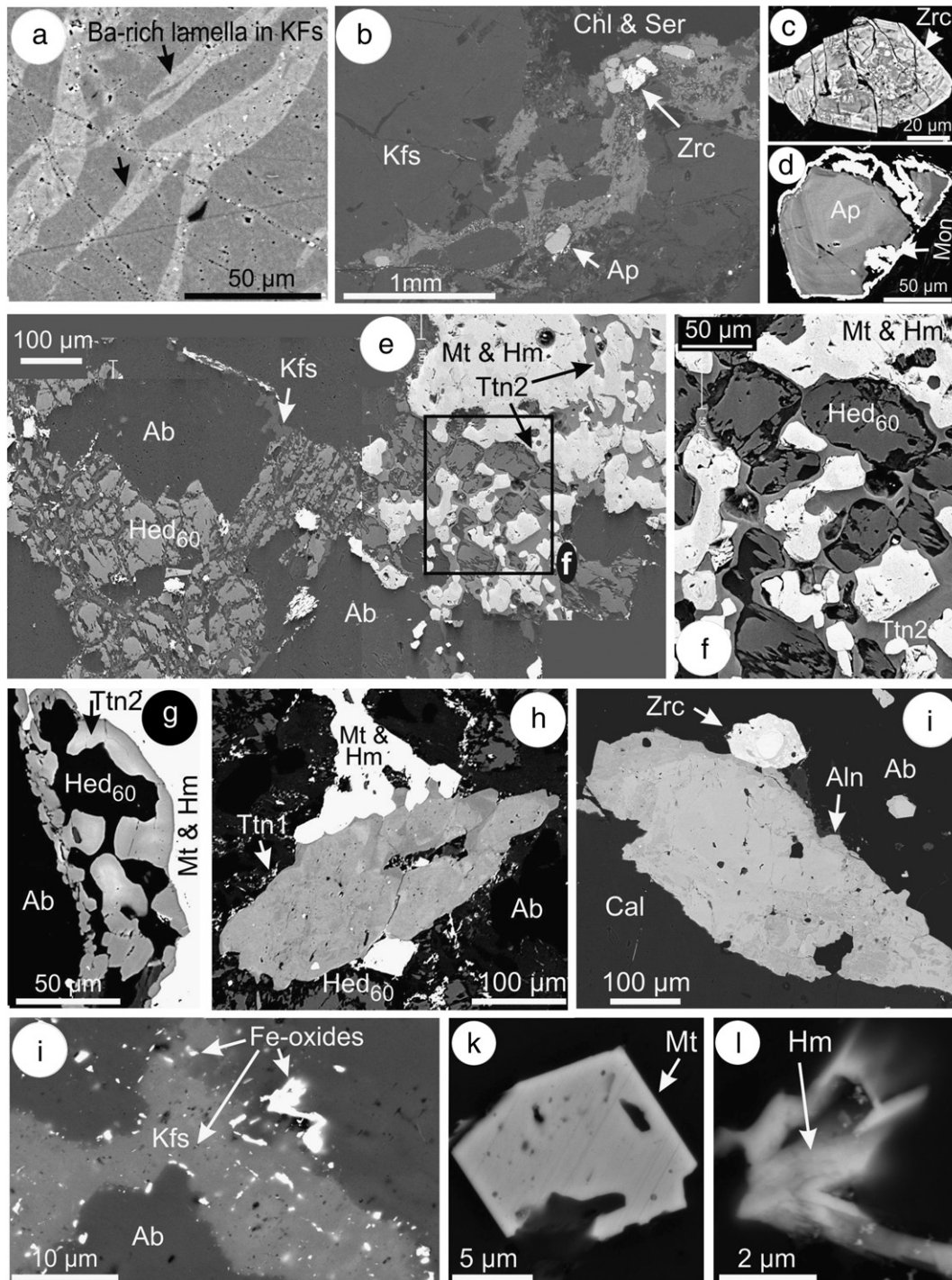


Fig. 4. Back-scatter electron (BSE) images showing aspects of Hillside granite (a–d; 26HS) and early feldspar–pyroxene skarn (e–l). (a) Ba-rich lamellae in orthoclase. (b) Abundant accessories along bundles of chlorite + sericite resulting from alteration of mafic minerals. (c and d) Zircon and apatite, respectively, affected by hydrothermal alteration; the latter preserves a zoned magmatic core. (e) Typical relationships between pyroxene (Hed₆₀), albite and Fe-oxides in early skarn (7HS). (f and g) Disequilibrium relationships between pyroxene and interstitial titanite (Ttn-2; 7HS and 24HS). (h and i) Typical coarse, sub-euhedral and zoned accessories (Ttn-1 and allanite, respectively) in early skarn (7HS), preserving a late-magmatic signature. Note the presence of small zircon in (i). (j) Dusty Fe-oxide inclusions underlining relationships between K-feldspar and albite in early skarn (24HS). (k and l) Detail of magnetite and hematite, respectively, from fields of dusty inclusions as in (j). Abbreviations: Ab—albite, Aln—allanite, Ap—apatite, Cal—calcite, Chl—chlorite, Hed—hedenbergite, Hm—hematite, Kfs—K-feldspar, Mon—monazite, Mt—magnetite, Ser—sericite, Ttn—titanite, Zrc—zircon.

attributable to either K-feldspar (relics) or calc-silicates. Magnetite, extensively replaced by hematite, minor chalcophyrite and abundant titanite characterize such intensely-altered feldspar skarn.

Feldspar–pyroxene skarn, particularly the albite dominant sub-type, is considered early relative to the other skarns based on the inherited ‘magmatic’ features as described.

5.3.2. Garnetites

Although garnet is an abundant component of most calcic skarns, we separate massive garnet (*garnetite*) as a distinct type. Garnet shows no compositional zoning in BSE-images, is fractured and replaced by chlorite, calcite and quartz. All samples contain not only Fe-oxides but also pyrite and chalcophyrite. Garnets also occur as fragments, often outlined

by quartz–calcite selvages within chalcopyrite. Apart from pervasively replacing magnetite, hematite also occurs as lamellar aggregates within chalcopyrite. Accessory minerals are conspicuously absent in samples we analyzed.

5.3.3. Multicomponent calcic skarns

Multi-component pyroxene–garnet–clinozoisite–actinolite skarns are most common; they are variably garnet-, pyroxene- or clinozoisite-dominant. For simplicity, these will be called ‘calcic skarns’. Patches or bands of mineralogically-different varieties are present on a variety of scales; all contain feldspars. The latter, in particular K-feldspar, appears texturally as relicts. Replacement of K-feldspar by albite is observed; both are heavily replaced by fine intergrowths of calcite–quartz. Both un-zoned and zoned garnet can coexist in the same sample. The latter displays compositional oscillatory and core-to-rim zonation, with Fe-rich cores. They often form rings around relict pyroxene (Fig. 5a) or calcite and can be replaced by clinozoisite (Fig. 5b).

Fronts of oscillatory-zoned Al-rich garnet (Fig. 2), repetitively banded with, and grading into clinozoisite are observed (25HS). Oscillatory-zoned garnet is also found within late calcite veins crosscutting marble-ore assemblages (19HS). Both cases are interpreted as distal skarns but only in the context of a local contact to protolith, either Al-rich MW rocks or marble formed on behalf on an impure carbonate.

Replacement of diopside by clinozoisite (Fig. 5c) and actinolite (Fig. 5d) is also common. Only rarely is actinolite observed without

pyroxene (Fig. 5e). Abundant accessories, in particular lozenge-shaped titanite, and apatite (often together), are observed in the calc-silicate mass; titanite is also abundant within Fe-oxides (Fig. 5f). Titanite and apatite display no, or only weak internal zoning but may be fractured, and in some cases replaced by clinozoisite, quartz and calcite.

Coarse pyrite occurs throughout the calcic skarns and often contains rounded inclusions of chalcopyrite and pyrrhotite (interpretable as products of *intermediate solid solution*). Pyrite is mostly brecciated, and associated with, or in-filled by chalcopyrite (Fig. 5g). Small garnet with Al-rich rims, together with needles of actinolite, occurs within chalcopyrite or at boundaries between opaques (Fig. 5g). Grains of native gold and/or tellurides (e.g., altaite), a few μm in size, are observed at pyrite–chalcopyrite boundaries (Fig. 5h–j). Minor ore minerals include galena–clausthalite solid-solution, hessite, cassiterite and arsenopyrite. In our sample suite, the ore-stage is defined by the presence of chalcopyrite associated with minerals characteristic of intense hydrothermal alteration (calcite, quartz and chlorite) replacing pre-existing minerals, including skarn silicates. This pervasive replacement of skarn is associated with precipitation of chalcopyrite and late hematite.

Hematite is most abundant as pseudomorphs after magnetite. However, a new generation of lamellar hematite is observed in samples with abundant pyrite and chalcopyrite that have obliterated skarn minerals (5HS; Fig. 5k).

Broadly, we interpret relationships between garnet and pyroxene as defining the prograde stage whereas clinozoisite and/or actinolite

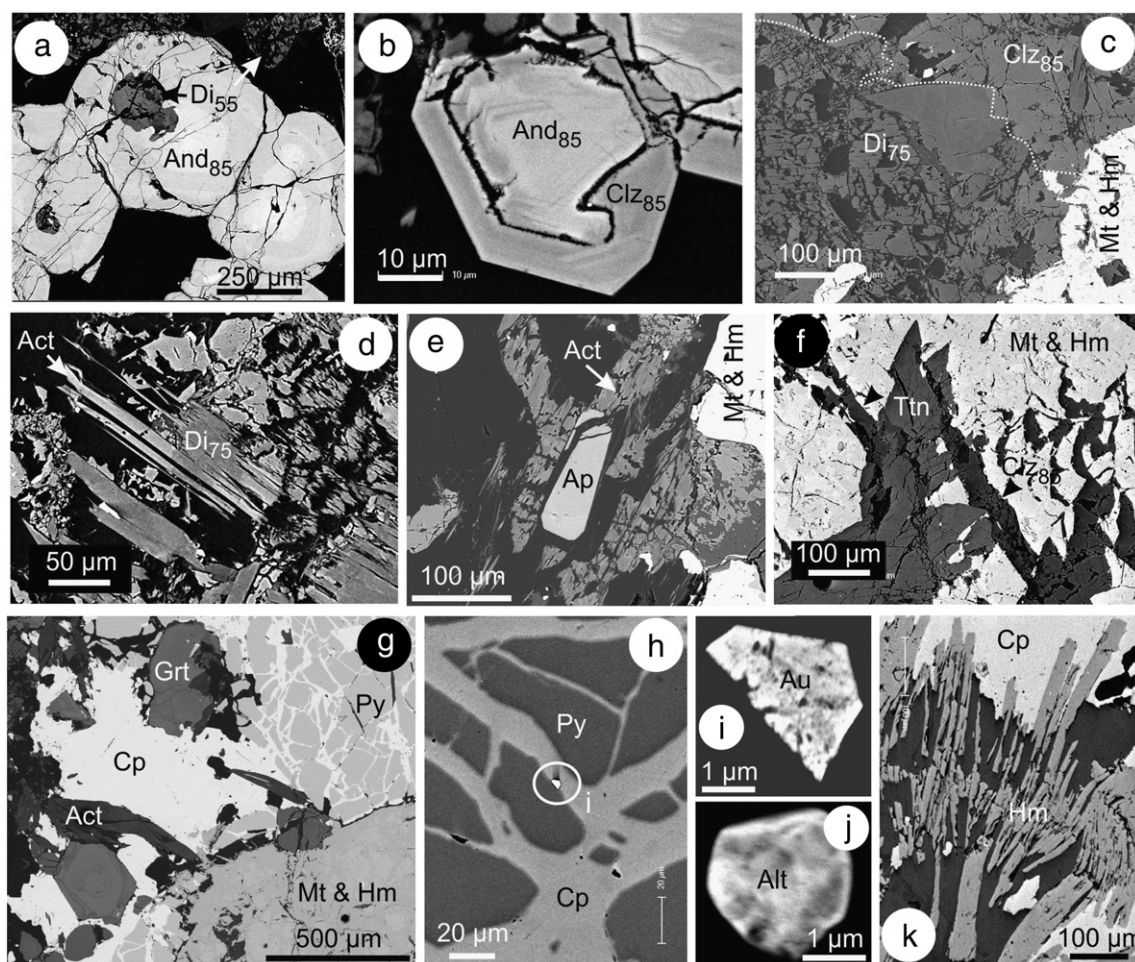


Fig. 5. BSE images showing skarn and ore petrography. (a and b; 4HS) Compositionally-zoned garnet grown onto a pyroxene core, and garnet replaced by clinozoisite, respectively. (c and d; 3HS). Replacement of diopside by clinozoisite and actinolite, respectively. (e) Brecciation of apatite enclosed within actinolite (18HS). (f) Lozenge-shaped titanite within Fe-oxides typical of calcic skarn; note replacement by clinozoisite (3HS). (g) Brecciated pyrite associated with and in-filled by chalcopyrite. Note small garnet and actinolite growth within sulfides. (h–j; 4HS) Native gold and tellurides at pyrite–chalcopyrite boundaries. (k) Late, lamellar hematite crosscutting pyrite–chalcopyrite boundaries (5HS). Abbreviations as in Fig. 4 and: Act–actinolite, Alt–altaite, And–andradite, Au–native gold; Clz–clinozoisite, Cp–chalcopyrite, Di–diopside, Grt–garnet, Py–pyrite, Ttn–titanite.

represent retrograde overprinting. We cannot however rule out that some clinozoisite is prograde, e.g., in repetitive banding with Al-rich garnet. Conversely, garnet could have grown during the retrograde stage (e.g., Fig. 5g). Magnetite, titanite and apatite appear to be mostly part of the prograde association whereas hematite is clearly retrograde, either replacing magnetite, predating chalcopyrite precipitation (Fig. 4d), or following chalcopyrite (Fig. 5k). However, titanite and apatite, brecciated during mineral replacements defining the retrograde stage (Fig. 5e, f), continued to form during post-skarn stage, i.e., ore deposition. The paragenetic position of pyrite is consistent with prograde deposition together with magnetite, but pyrite formation clearly continued into the retrograde- and ore-stages.

6. Microanalytical data for REE, Y and other trace elements

Nine minerals in the rocks hosting the Hillside mineralization were analyzed. Each shows a range of characteristic patterns for REE + Y (hereafter REY). To some extent, these patterns reflect typical, predictable patterns for each mineral, with trends and LREE/HREE fractionation controlled by crystal structural parameters intrinsic to each mineral group.

The majority of minerals analyzed in this study are from skarn minerals. We have, however, undertaken a preliminary assessment of REY concentrations and trends in feldspar and calcite. Although seldom hosting high concentrations, they are often some of the most volumetrically abundant minerals. Moreover, if well understood in a petrogenetic context, REE patterns of feldspar are important for discriminating signatures of 'protoliths' from signatures resulting from hydrothermal processes. We address the accessory minerals in some detail since they are major REY repositories at Hillside.

We include Y in tables and figures, positioning the element between Dy and Ho, following practice elsewhere (e.g., Bau, 1996). Σ REY is defined as the sum of measured (La + Ce + Pr + Nd + Sm + Eu + Gd + Tb + Dy + Y + Ho + Er + Tm + Yb + Lu). Normalization to chondrite follows McDonough and Sun (1995).

All three major skarn minerals concentrate REY (Fig. 6). Garnet has some of the highest REY concentrations, notably within Zanoni garnetites. Pyroxene (and the replacing actinolite) contains lower Σ REY than garnet or clinozoisite in calcic skarn.

6.1. Feldspar

The LA-ICP-MS dataset for 9 feldspar-bearing samples (Electronic Appendix C1, Fig. 7) shows that Σ REY is at best a few ppm, lower than for all other minerals. Aside from skarn, two main, potential protolith lithologies contain major component K-feldspar as: red-rock and Hillside granite. These two sub-populations give the most consistent chondrite-normalized patterns for feldspar, displaying similar REE patterns with La-enrichment and consistently strong positive Eu-anomaly, concordant with published data (e.g., Bea, 1996). Feldspars in the Hillside granite do, however, also show strong negative Y-anomalies, whereas those in the red-rock do not. K-feldspar in the hydrothermally-altered granite (23HS) is very similar to the unaltered granite. REE patterns do not show any correlation with the Ba-enrichment described above.

K-feldspar in feldspar-pyroxene skarns and hydrothermally-altered samples shows different trends. They retain the positive Eu-anomaly but display no Y-anomaly. K-feldspar in feldspar-pyroxene skarns (24HS) shows strong LREE-enrichment and a downwards-sloping REE trend. In contrast, feldspar from ore-stage skarn (5HS) is characterized by HREE-enrichment. Two trends that are substantially different are seen in skarn with large relict feldspar (8HS) and also in the green MW rock with coarse clinozoisite (15HS). These trends (similar to granite or red-rock with a strong negative Y-anomaly but no pronounced Eu-anomaly) suggest that the K-feldspar in calcic skarn is inherited from precursor rocks (banded MW calc-silicate-feldspar rocks).

Albite from albite-dominant pyroxene skarn (7HS) shows a trend with a strong negative Y-anomaly, very similar to trends shown by K-feldspar in skarns with relict MW signature. Albite in calcic skarn shows a somewhat similar pattern, albeit with a less pronounced Y-anomaly.

A ternary Rb–Ba–Sr plot (Fig. 8a) shows that K-feldspar in the MW red-rock is distinct from that in the Hillside granite in terms of trace elements, backing up the distinct character of feldspar in each rock on the REE patterns. K-feldspar in the MW red-rock builds a tight cluster along the Ba–Rb edge, closer to Ba, whereas the Hillside granite is higher in Rb, and displays a greater spread, extending towards the Sr-apex. Albite from early pyroxene skarn plots in the Sr corner. K-feldspar from calcic skarn plots between the Hillside granite and MW red-rock. The Ba/Rb ratio of K-feldspar in granites is ~1 (MW red-rock: ~3; calcic skarn: ~2).

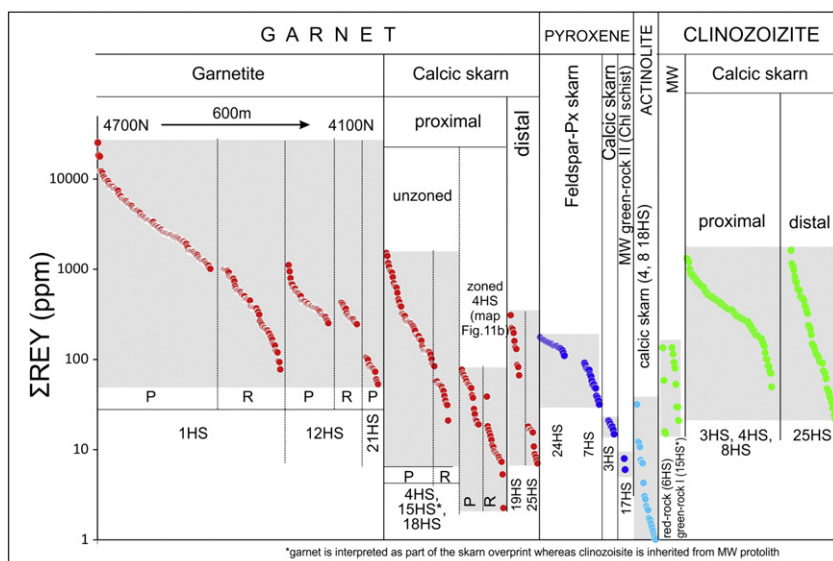


Fig. 6. Cumulative frequency plot of Σ REY in garnet, pyroxene, actinolite and clinozoisite from different skarn associations. P—prograde, R—retrograde.

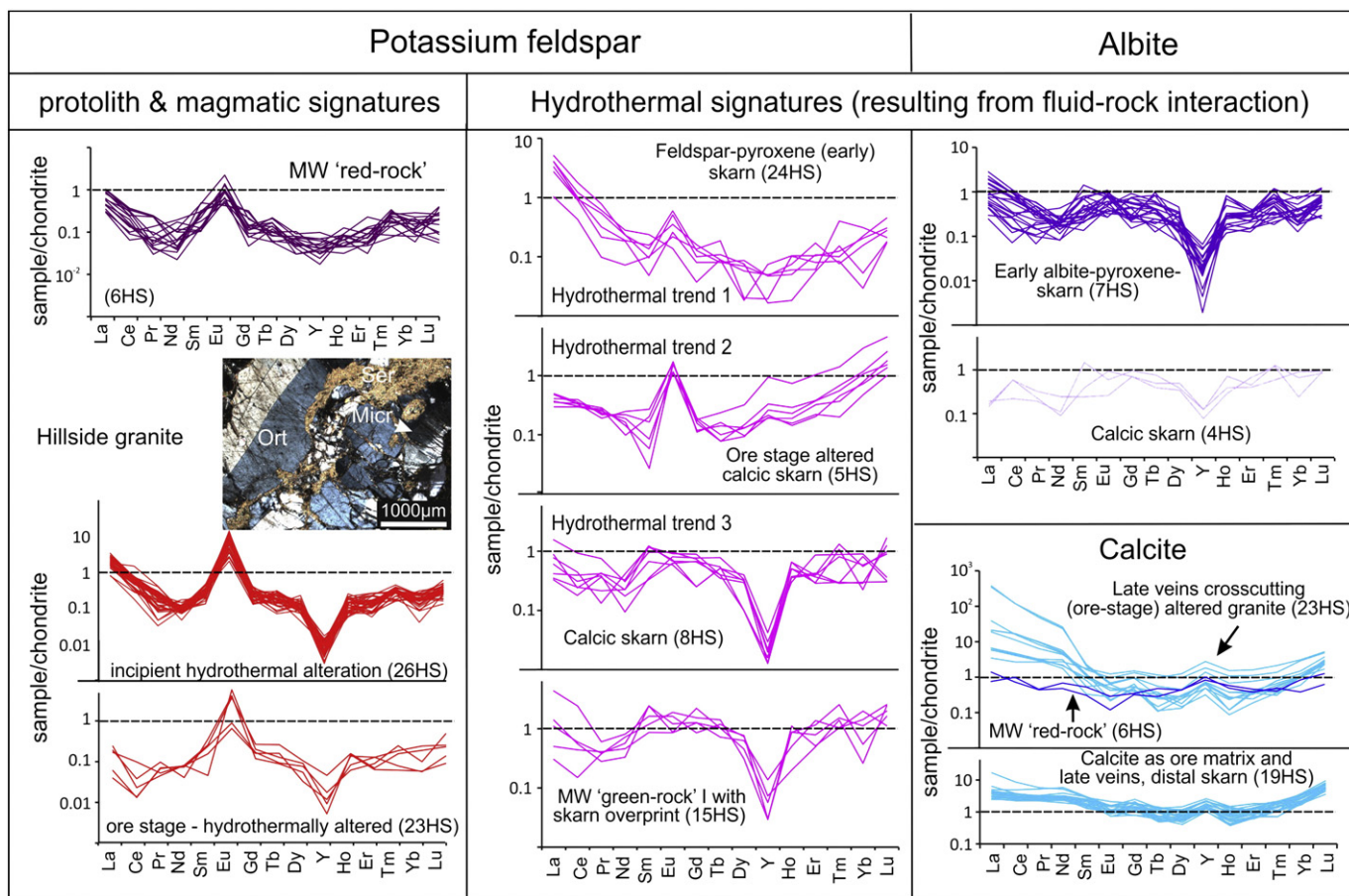


Fig. 7. Chondrite-normalized REY plots for K-feldspar, albite and calcite. See text for explanation.

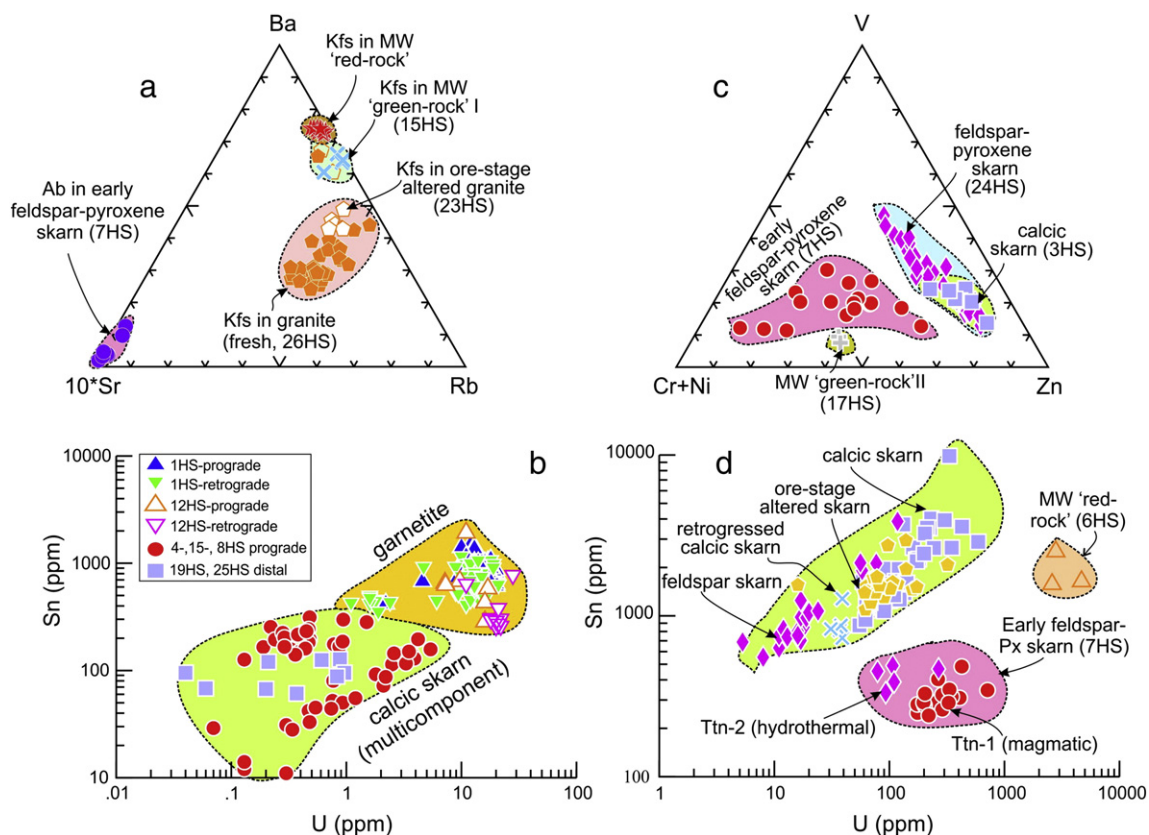


Fig. 8. (a) Ternary Rb–Ba–(Sr*10) plot for K-feldspar and albite. (b) Plot of Sn vs. U in garnet. (c) Ternary (Cr + Ni)–V–Zn plot for pyroxene. (d) Plot of Sn vs. U in titanite.

Similarly, U/Th ratios in feldspar are significantly higher in the MW red-rock (7–90 ppm) than in granite (mostly <5 ppm) or calcic skarn. K-feldspar in the granite is, however, enriched in Cs (2–3 ppm) relative to MW red-rock (1–1.5 ppm); values for the skarns lie between the two. Albite consistently contains <0.1 ppm Cs. The MW red-rock is characterized by a wide range of Hf/Lu (2–30); other lithologies show narrower ranges in which Hf/Lu seldom exceeds 5.

6.2. Calcite

Carbonates can incorporate REY, providing information on processes influencing mineral formation and growth (e.g., Charniak, 1998). Coarse-grained calcite was analyzed from veins in altered granite and the red-rock. Both sub-populations show measurable REY concentrations and consistent trends with modest positive Y-anomalies. Late veins in the altered granite also display significant LREE-enrichment in calcite (Electronic Appendix C2, Fig. 7). Calcite from the ore matrix and late veins in distal skarn (19HS) shows similar REY patterns to the veins in the red-rock.

Calcite carries a few tens to low hundreds of ppm Sr but is a poor host for Rb or Ba. Ore-stage calcite displays Mn-enrichment (mean 7800 ppm).

6.3. Garnet

Garnet is defined as $X_3Y_2Z_3O_{12}$, where X is a divalent cation (Ca, Mg, Mn or Fe^{2+}) in eight-fold, dodecahedral coordination, Y is the trivalent cation site (Fe^{3+} , Al or Cr) in octahedral coordination and Z is Si in tetrahedral coordination. Incorporation of $(Y, REE)^{3+}$ by replacement of X^{2+} cations requires coupled substitution to maintain charge balance. Three mechanisms are advanced: 'yttrigarnet' (YAG)-type substitution involving charge balance by substitution of a trivalent cation into the Z (Si) site (Jaffe, 1951); incorporation of a monovalent cation (essentially Na^+) into the X site (Enami et al., 1995) or; charge compensation via vacancies in the dodecahedral site. Carlson (2012) discusses these alternatives, but favors a fourth, recently proposed mechanism in which charge balance is achieved by substitution of divalent cations (Mg^{2+} , Fe^{2+}) into the Y site (as in menzerite; Grew et al., 2010).

Data for 9 garnet-bearing samples show Σ REY concentrations in garnet from garnetite or calcic skarn span up to 3 orders of magnitude, from tens of ppm up to approaching 1 wt.% (Electronic Appendix C3, Fig. 6). REY patterns in garnetites vary from some of the highest to concentrations that are orders of magnitude lower, e.g., in garnet from late calcite veinlets (19HS). There is a clear decrease in Σ REY concentrations in garnet over the 600 m-long N–S strike of our sampling, i.e., from the Zononi zone in the northern part of the deposit (1HS), to the Parsee zone (21HS) (Fig. 6), from prograde to retrograde stages, and in general, from proximal to distal skarn.

REY patterns for all samples except distal skarn and oscillatory-zoned grains are characterized by relative LREE-depletion (La–Pr), and a 'jump' to a flattish pattern from Sm to Ho, and, in most cases, an upwards-sloping Ho–Lu segment (Fig. 9). There is variation in the patterns not only with respect to N–S location in the system, but also prograde (trend 1; T1) to retrograde stage (trend 2; T2), or the presence or absence of oscillatory compositional zoning with respect to major components (Fe and Al) (trends 3 and 4; T3, T4). Garnet from distal skarns (19- and 25HS) display a peculiar, relative LREE-enrichment (trend 5; T5). Hillside garnet is a significant repository for Y, with positive Y anomalies of variable size.

Prograde garnet from garnetites varies in the steepness of slope with marked HREE-enrichment in the north (1HS) to modest further south (12 HS, 21 HS). Similar, upwards-sloping HREE-enrichment is seen in garnet from multi-component skarns, although Σ REY is up to an order of magnitude lower (4HS). However, in the latter, different trends co-exist, as observed in garnets with pronounced oscillatory zoning and those without (4HS). In the zoned case, there is an overall depletion

in Σ REY, particularly in the Gd–Ho segment, and a strong positive Eu-anomaly, comparable only to that in the distal skarn (25HS).

Grain-scale trace element distributions in garnetites (Zononi zone; 1HS and 12HS) with no Fe- and Al-zonation were mapped by LA-ICP-MS. In sample 1HS, distributions (Fig. 10a) reflect two types of patterns: a fine oscillatory zoning pattern for minor elements such as Ti and Y, mimicked by REE and incompatible elements (Sc, V and Nb); and; secondly, a pattern of brecciation reflected by Al and Sn (the latter present at concentrations of ~1000 ppm). The patterns reflect two growth cycles: a deformed core; and a marginal zone. Some elements (Ti and V) appear depleted in the deformed core relative to the margin.

Similar to the above, garnets in sample 12HS show little zoning in terms of major elements (e.g., Al) but a strong zoning of REY and incompatible elements (V, Y, Nb; Fig. 10b); there is no obvious deformation. In contrast to 1HS however, Th but not U shows pronounced zoning. Tin (not shown on the figure) also shows no pattern although concentrations are some hundreds of ppm.

REY trends obtained from garnetite, either brecciated grains, or garnet fragments incorporated within chalcopyrite, can be interpreted as retrograde in origin (T2). Such garnets (sub-populations in 1HS and 12HS) are characterized by relative MREE- and HREE-depletion. In 12HS, the patterns show no Eu-anomaly, and a characteristic 'rounded' transition between LREE and MREE. Grain-scale maps for garnet embedded in chalcopyrite (1HS; Fig. 11a) strongly support the interpretation that they represent fragments that underwent partial recrystallization during the retrograde stage. We note the oscillatory zonation shown by all elements in the central part of the fragment, highlighted by Mn, Al, Sn and Ta, and depletion of Ti, REE, Y and U in the core relative to the margins. We interpret the central part as having recrystallized based on comparison with the massive part of the same sample.

Oscillatory-zoned garnet from multi-component skarn (4HS) showing distinct T3 and T4 REY trends (Fig. 9d) was also mapped. In this case a correlation between the zonation trends shown by Fe and Al, and minor/trace components (Mn, REE) is observed (Fig. 11b). A similar correlation between major elements, Y and Sn is observed for oscillatory-zoned garnet from distal skarn (T5).

Tin-enrichment (Figs. 10a and 11a) and the oscillatory character of Sn distribution on element maps of garnet from late calcite veins are conspicuous.

The element maps underline that garnet also hosts significant Ti, V, Zr, Nb and U. A binary Sn vs. U plot for garnet (Fig. 8b) shows that both elements are enriched and that they correlate positively with one another. Both elements are clearly higher in garnetites relative to multi-component skarn. The relative absence of accessories or other skarn minerals in the garnetite could explain these distributions.

6.4. Pyroxene

REE incorporation into pyroxene, $XY(Si, Al)_2O_6$, involves replacement of Ca^{2+} in the X-site by REE^{3+} . To achieve charge balance, coupled substitution involving vacancies has been proposed (e.g., van Orman et al., 2001), as well as coupled substitution involving monovalent cations (e.g., Na^+). We note conspicuously high Na_2O concentrations in all analyzed pyroxenes (1–2 wt.%). The presence of Al_2O_3 might also suggest charge balance via compensation for REE^{3+} incorporation into the Ca site by Al^{3+} incorporation into the Si site.

LA-ICP-MS trace element data on 4 samples suggest that skarn pyroxenes are also significant REY hosts, especially when garnet or clinozoisite are absent (Electronic Appendix C4, Fig. 12). Concentrations are lowest in cases where clinozoisite is abundant. Σ REY is, however, lower than in garnet, reaching maxima of tens to hundreds of ppm (Fig. 6).

In feldspar–pyroxene skarn, concave REY patterns display HREE-enrichment, negative Eu-anomalies, and slight variation in the La–Pr segment. REY concentrations are highest in K-feldspar-dominant skarn (24HS). Pyroxenes from calcic skarn (Σ REY tens of ppm) show

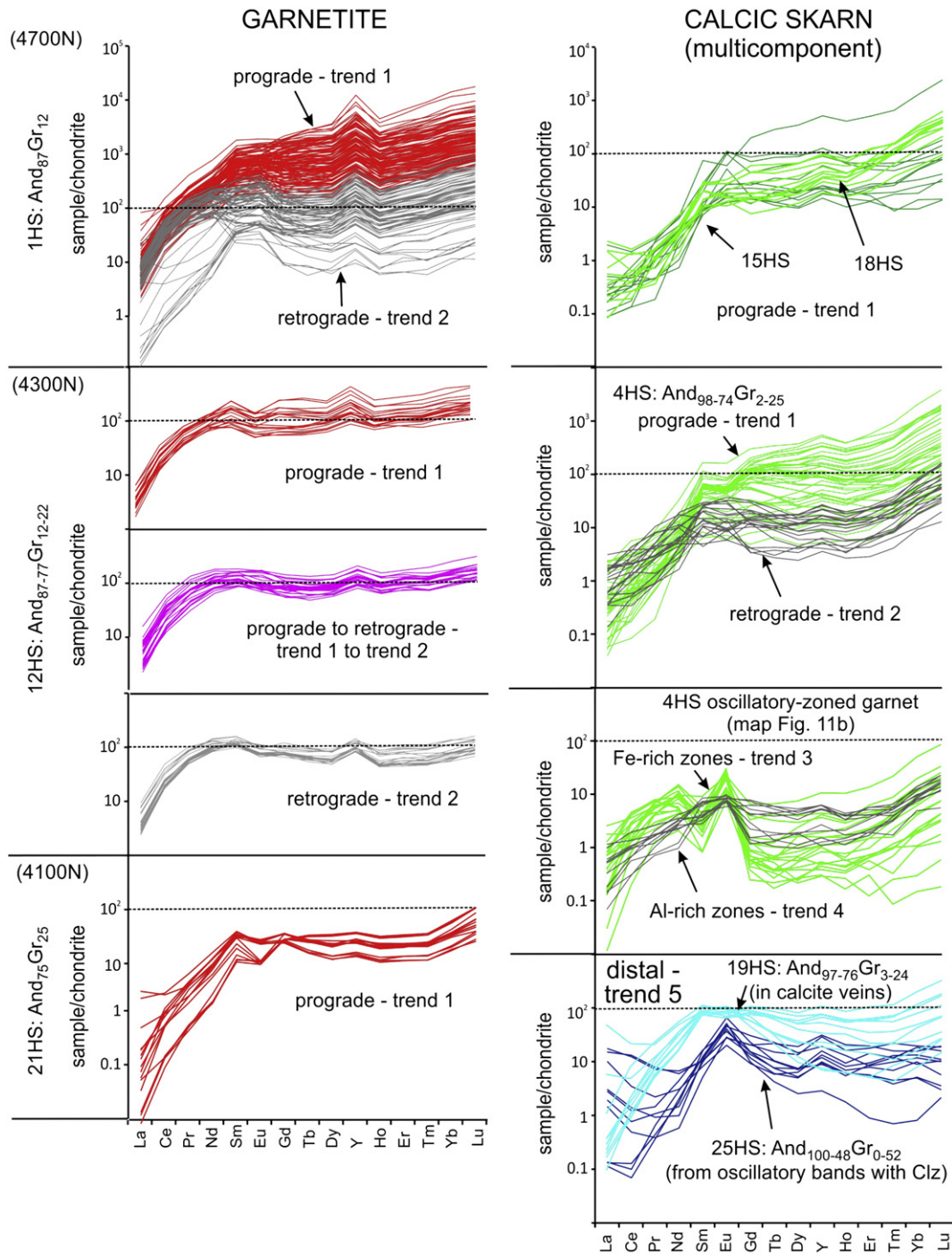


Fig. 9. Chondrite-normalized REY plots for garnet. See text for explanation.

flatter trends up to Er relative to feldspar-dominant skarn but similar HREE-enrichment and negative Eu-anomalies. Pyroxene inclusions in pyrite from chlorite schist (17HS) have much lower Σ REY (a few ppm) which display a very different pattern characterized by enrichment in LREE relative to HREE and a strong negative Y-anomaly.

Pyroxene will typically carry a few tens of ppm Co and Zn, as well as a few hundred ppm Ti and Cr. A ternary (Cr + Ni)–V–Zn plot for pyroxene (Fig. 8c) shows distinct fields in which pyroxene in early skarn (7HS) shows a spread but is positioned towards the (Cr + Ni) apex. In contrast, pyroxene from K-feldspar-dominant skarn forms a trend closer to the V–Zn line, overlapped by pyroxene from multi-component skarn; the latter is notably richest in Zn.

6.5. Actinolite

Amphibole-forming reactions are essentially isochemical and REY concentrations in amphibole replacing pyroxene are typically at similar levels, or lower, than in pyroxene (e.g., Mulrooney and Rivers, 2005). REE incorporation in calcic amphibole occurs via substitution into the M4 (Ca) site ($\text{Ca}^{2+} + \text{Si}^{4+} \leftrightarrow \text{REE}^{3+} + \text{Al}^{3+}$). Evidence for a two-site model has, however, been proposed (Bottazzi et al., 1999), in which the larger LREE are preferentially incorporated at the M4 (Ca) site but the smaller HREE are primarily located at the M4' (Fe,Mg) site.

Actinolite from 3 calcic skarns (Electronic Appendix C4, Fig. 12), in which it replaces pre-existing pyroxene, shows consistently

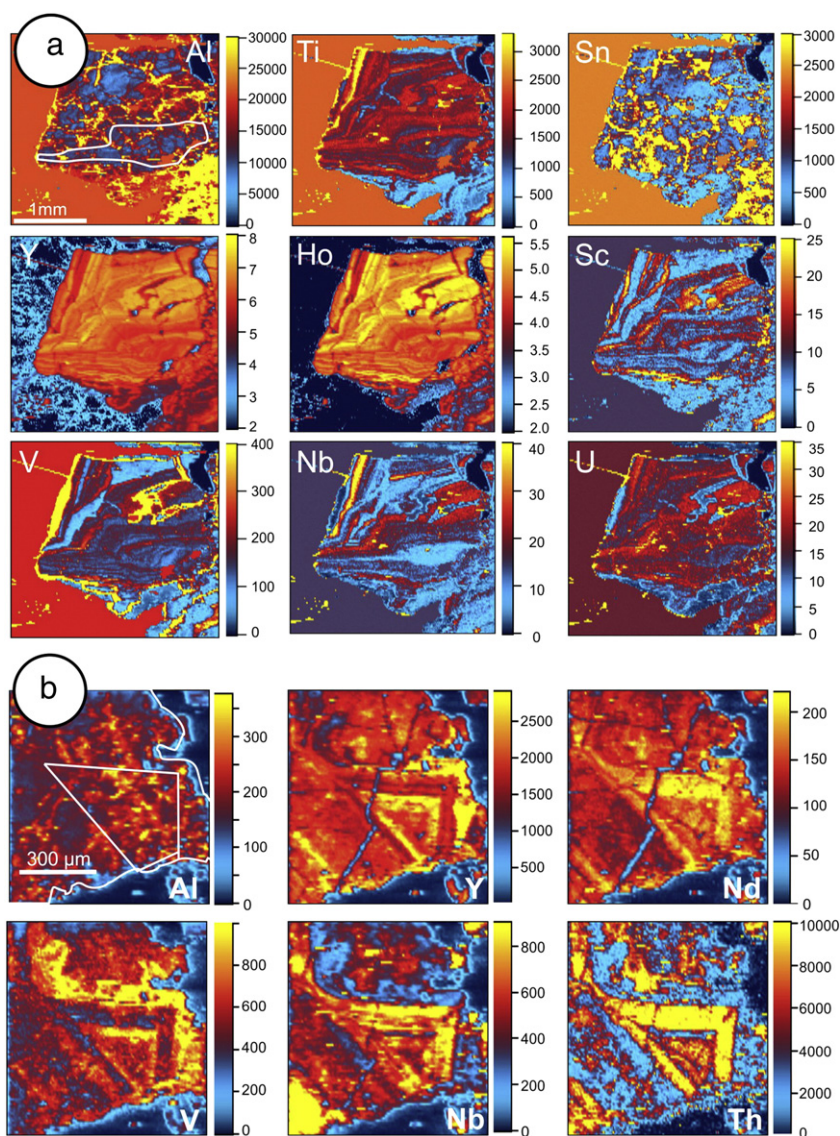


Fig. 10. LA-ICP-MS element maps for garnet in garnetites that are unzoned with respect to Fe and Al. (a) Superposition of oscillatory zoned patterns shown by Ti, REY, Nb, Ta, V, Sc, Zr and U. Outline on the Mn map shows a deformed core. Retrograde brecciation pattern is underlined by Al and Sn. (b) Oscillatory-zoned pattern shown by Ti, REY, V, Nb and Th. Outline on Al map highlights the lack of correlation between this element and the trace elements. On (a, 1HS) scales are in ppm, except for Y and Ho, which are counts-per-second (cps) on a log-scale, i.e., numbers on scale (n) represent 10^n . On (b, 12HS), scales in $\text{cps} \times 10^3$, except for Al ($\times 10^6$) and Th ($\times 10^1$).

lower $\sum \text{REY}$ (<10 ppm) but trends that are broadly similar to pyroxene. The patterns are, however, noisier with respect to Ce and Y (transiting from negative to slightly-positive anomalies) and without Eu-anomalies. The range of HREE concentrations is also broader than in precursor pyroxene. Concentrations of other trace elements are typically similar to, or lower than in pyroxene. Nickel and Zn are exceptions; both elements are enriched (tens to hundreds of ppm) in skarn actinolite.

6.6. Epidote-group minerals

Frei et al. (2004) show how epidote-group minerals, $\text{A}_2\text{M}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{O,F})(\text{OH})$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Pb}^{2+}, \text{Mn}^{2+}, \text{Th}, \text{REE}^{3+}, \text{U}$; $\text{M} = \text{Al}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Mn}^{3+}, \text{Mn}^{2+}, \text{Mg}, \text{Cr}^{3+}, \text{V}^{3+}$), incorporate REE as well as large-ion lithophile elements (LILE) and a range of other trace elements into the A site and the three nonequivalent octahedral sites, M1, M2, and M3. Monoclinic epidotes are represented by the clinozoisite–epidote solid-solution series, in which the $\text{Al}^{3+} \leftrightarrow \text{Fe}^{3+}$ substitution is continuous over a wide range of compositions. Allanite, $[(\text{Ca}, \text{Mn}, \text{Ce}, \text{La}, \text{Y})_2(\text{Fe}^{2+},$

$\text{Fe}^{3+}, \text{Al})_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O.OH}]$, is a relatively common accessory mineral in skarns and pegmatites, strongly fractionates LREE (Gieré and Sorensen, 2004) and typically exhibits a pronounced negative Eu-anomaly (e.g., Smith et al., 2009). Frei et al. (2004) discuss how the REE patterns from contact metamorphic and skarn environments display great variability with respect to slope and sense of Eu-anomaly.

The LA-ICP-MS dataset for clinozoisite from 6 samples of calcic skarn (Electronic Appendix C5) contains remarkably consistent concentrations of REY (mean $\sum \text{REY}$: 300–400 ppm; Fig. 6). Lower total concentrations are measured in clinozoisite replacing K-feldspar in the red-rock (6HS, mean $\sum \text{REY}$: 233 ppm), and markedly lower for coarse clinozoisite in MW green-rock (mean $\sum \text{REY}$: 90 ppm, 15HS). Clinozoisite from both proximal and distal skarns shows similar ranges of $\sum \text{REY}$, although this decreases in some distal skarns.

Clinozoisite from both proximal and distal calcic skarn is characterized by changes in the sign of the Eu-anomaly from negative to positive in the same sample (Fig. 13). In contrast, the REY pattern in the two potential protoliths shows no Eu-anomaly. Despite this, all analyzed clinozoisite shows comparable, LREE-enriched patterns, and slight

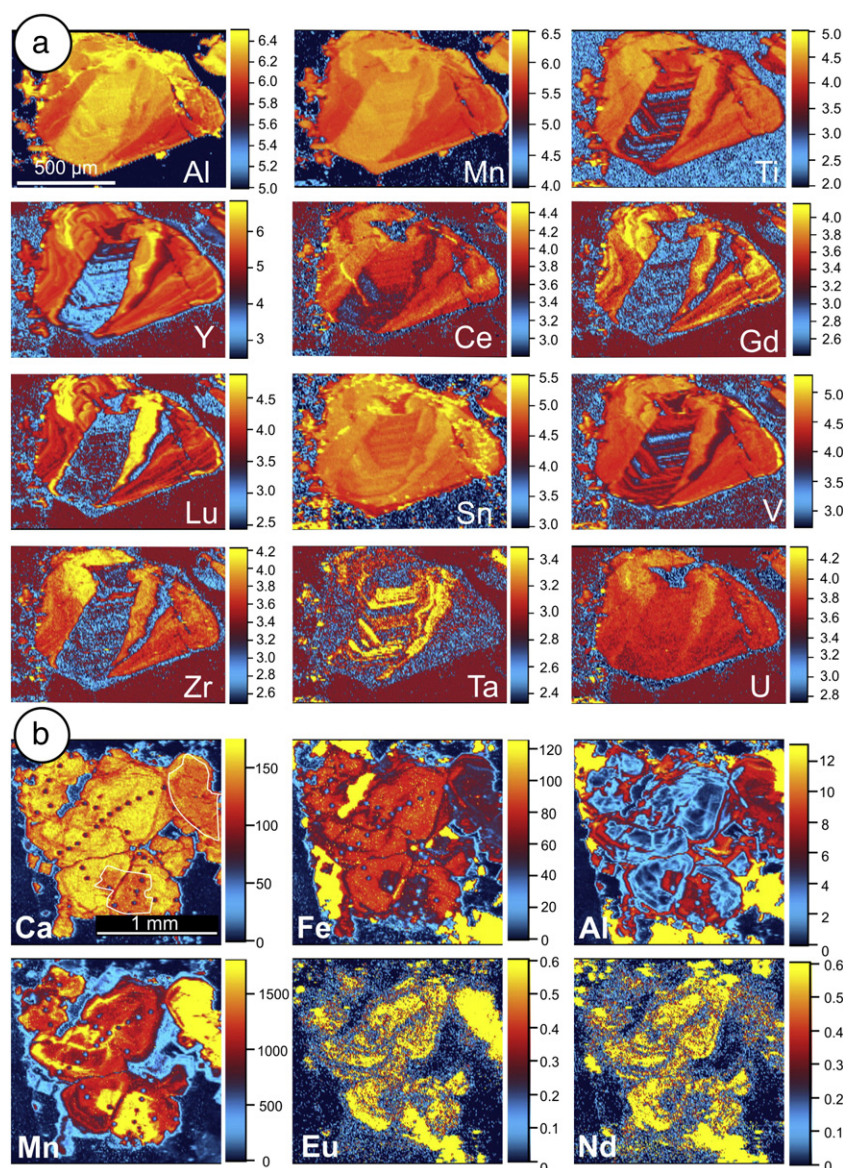


Fig. 11. LA-ICP-MS element maps for zoned garnet. (a) Garnet in chalcopyrite with a central part showing zoning of Al and minor/trace elements attributed to retrograde recrystallization (1HS). (b) Correlation between Fe/Al zoning and minor/trace elements in prograde garnet (4HS). Dark spots on (b) are ablation holes corresponding to trends 3 and 4 in Fig. 9. On (a), scales in cps on a log-scale (10⁹). For (b), scales in cps × 10³, except for Fe and Al (× 10⁹).

upwards slope towards HREE (except in distal skarn, 25HS). A further feature is the marked variation in $\sum$ REY over 1–2 orders of magnitude in most samples giving large standard deviations relative to means.

Apart from commonly reported, minor Cr and Ti, clinozoisite also contains minor but persistent concentrations of Zn, Ga and Rb.

LA-ICP-MS trace element data for allanite in 3 samples (Electronic Appendix C8, Fig. 14) shows similar negative Eu-anomaly but changes from a downwards-sloping pattern typical of magmatic signature in early skarn (7HS), to a concave, slightly upwards-sloping pattern for ore-stage altered samples (5HS and 23HS). These contrasting trends underline that allanite, like the other accessories, shows a marked change in REY patterns from magmatic to ore-stage.

LA-ICP-MS element maps of allanite in the two stages (Fig. 15) show internal heterogeneity with respect to REE and other elements. However, they differ markedly from one another in that, in the albite-dominant pyroxene skarn (Fig. 15a), heterogeneity reflects compositional zoning in terms of all LREE, as well as Mn, Ti, V, As, Pb, Th and U, suggestive of radial growth. Coarse, ore-stage allanite (Fig. 15b) features a very

different, patchy texture shown by all elements, which is interpreted as resulting from decomposition. A further feature of ore-stage allanite is the order of magnitude jump in Co, Zn and Sn concentrations in 5HS and 23HS, and drop in Ti and Cr, when compared to sample 7HS; Sc concentrations are also two orders of magnitude higher. Zirconium is elevated in sample 5HS but not in 23HS, possibly underlining a partly inherited signature in the latter. Other minor elements measured in all allanite grains include Na, Ga, Cu, Pb, Th and U. In contrast to titanite, allanite from early-skarn is lower in Sn, U and Zn.

6.7. Titanite

Titanite can play a major role in the REE distribution in igneous and metamorphic rocks. REE replace Ca via coupled substitution: $2\text{Ca}^{2+} + \text{Ti}^{4+} \leftrightarrow 2(\text{REE,Y})^{3+} + (\text{Al,Fe})^{3+}$, enhanced by additional $\text{Na} + \text{Ca}^{2+}$ exchange (Tiepolo et al., 2002). Titanite is also a major repository of HFSE (Ta^{5+} and Nb^{5+}), V, Zr and U (e.g., Frost et al., 2000; Tiepolo et al., 2002).

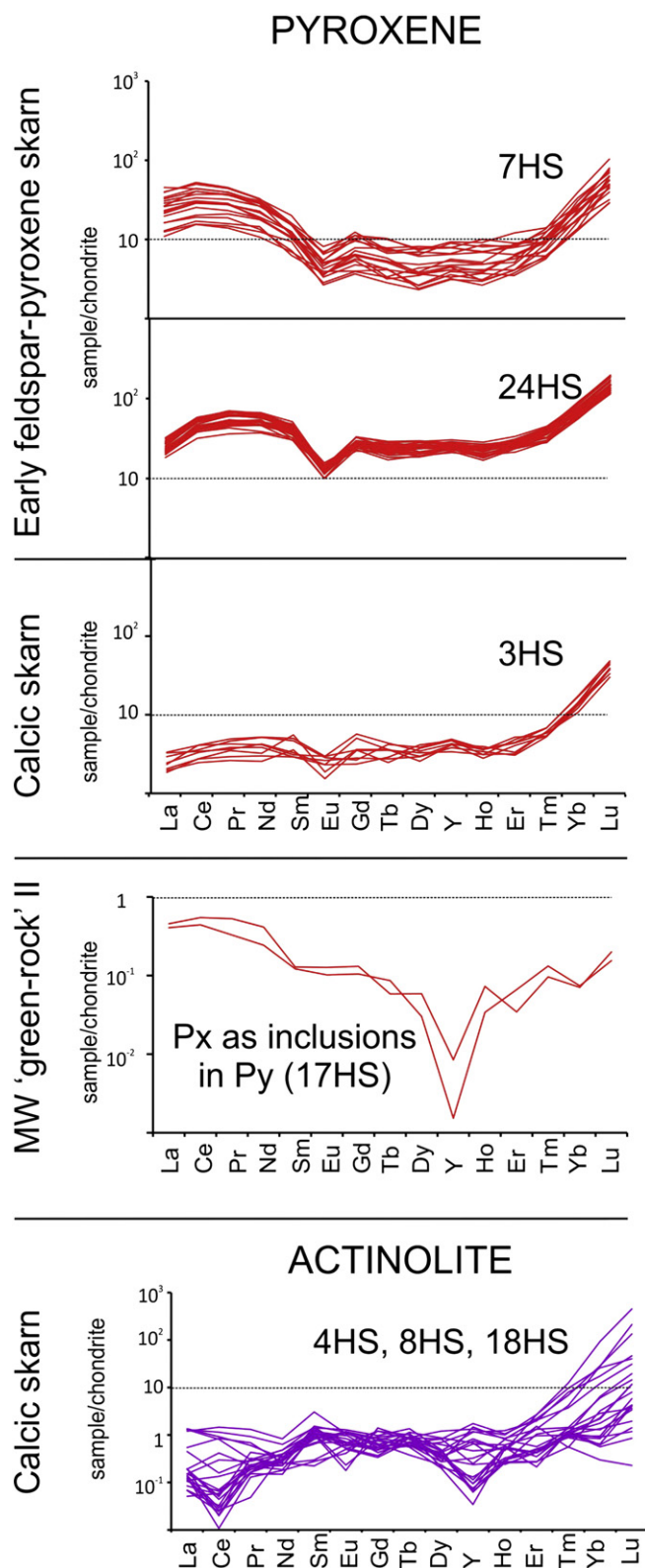


Fig. 12. Chondrite-normalized REY plots for pyroxene and actinolite. See text for explanation.

LA-ICP-MS trace element data were obtained for titanite in 11 samples covering skarns and MW 'red-rock' (Electronic Appendix C6, Fig. 14). Magmatic titanite in early skarn (Ttn-1) has the highest mean Σ REY (approaching 4 wt.%); prograde calcic skarns can attain up to 2 wt.%. In contrast, titanite from retrogressed skarn has lower

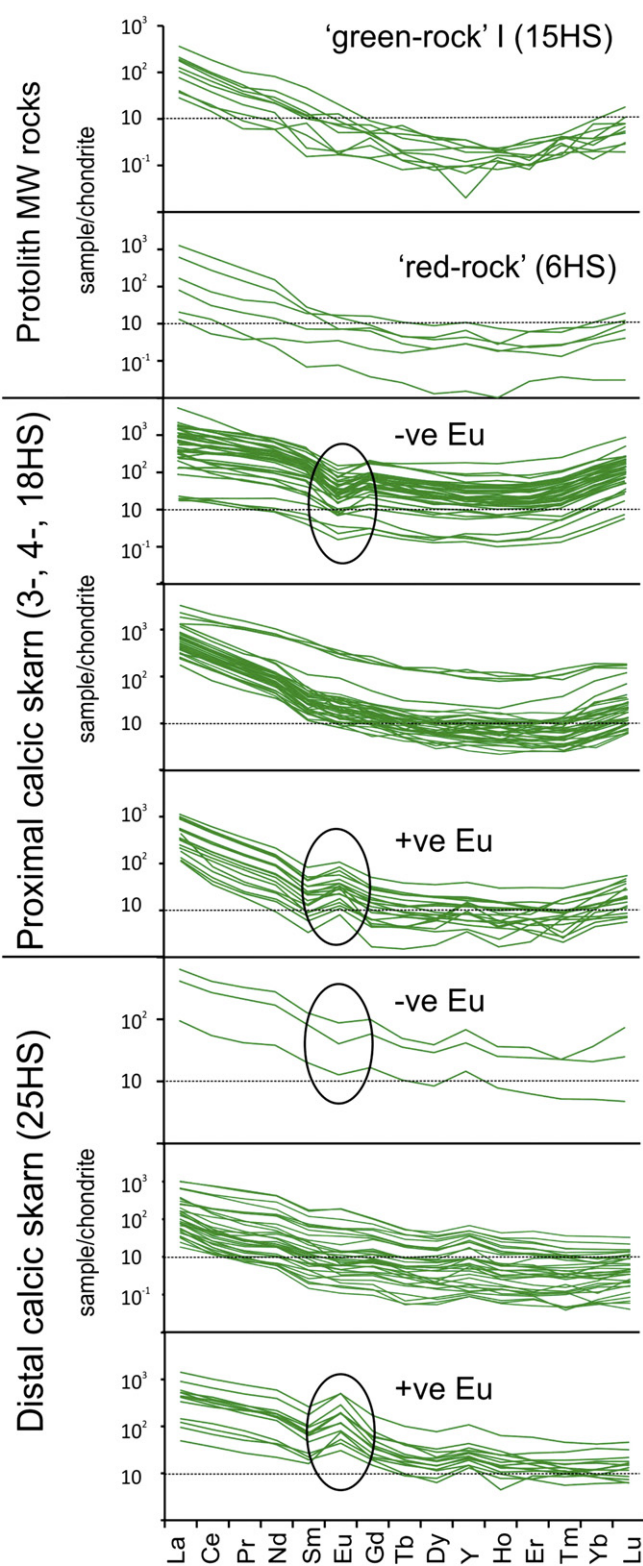


Fig. 13. Chondrite-normalized REY plots for clinozoisite. The change in the sense of Eu-anomaly, typical for this mineral even in the same sample is highlighted. See text for explanation.

concentrations, and titanite from the MW 'red-rock', one of the lowest (mean Σ REY 1165 ppm).

Titanites in 'red-rock' and feldspar skarns show similar pronounced convex patterns between La and Sm, but differ in the slopes of MREE–HREE. Magmatic Ttn-1 shows downwards-sloping trends for MREE–

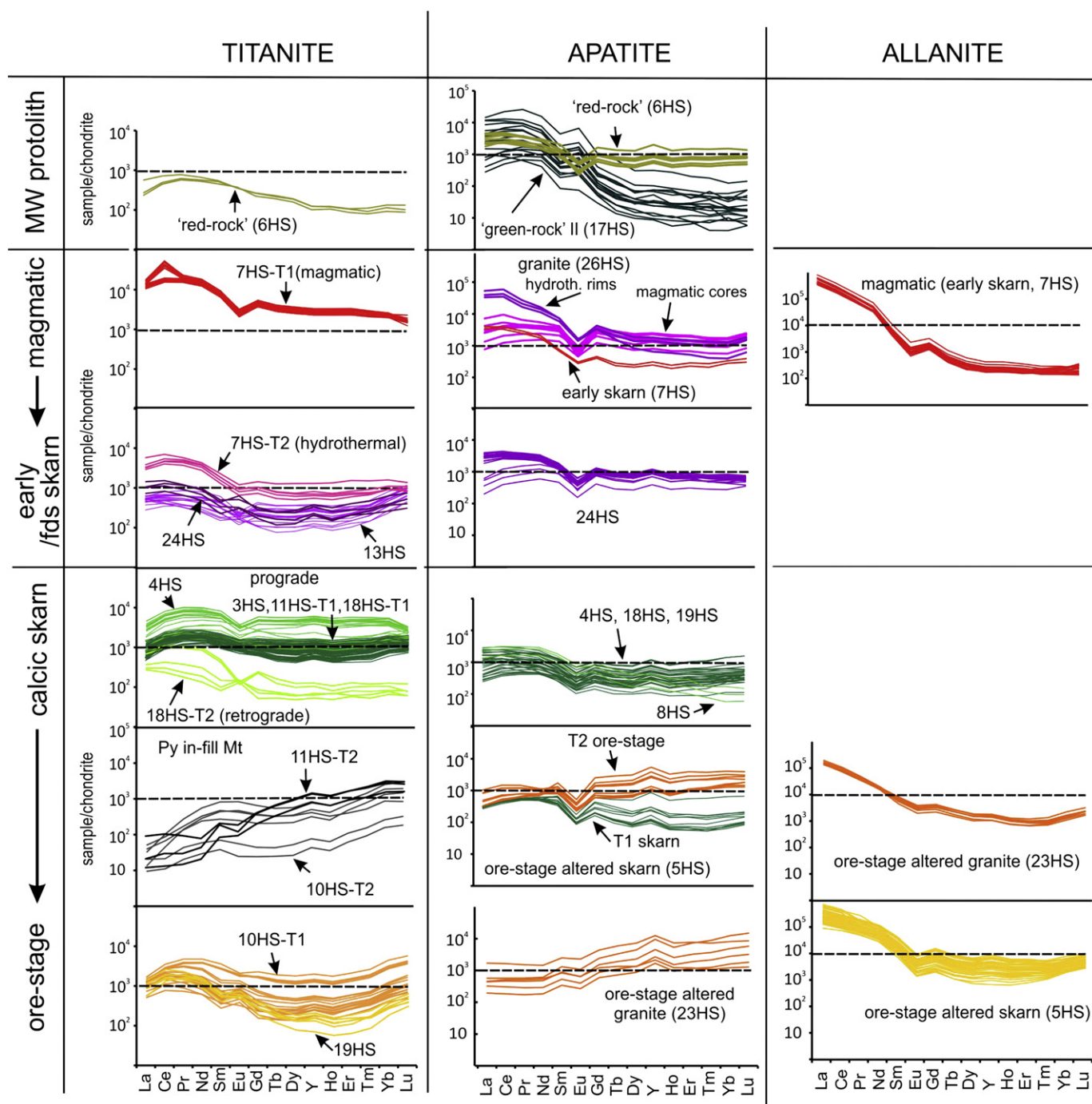


Fig. 14. Chondrite-normalized REY plots for accessories. See text for explanation.

HREE and hydrothermal titanite shows flat MREE–HREE. Magmatic titanite also has a pronounced negative Eu-anomaly; half the analyses in this group show a positive Ce-anomaly (Fig. 14). Titanite in 'red-rock' shows no Eu-anomaly and the size and sense of this anomaly vary for feldspar skarn samples.

Titanite in calcic skarn shows mostly consistent, flat REE patterns without Eu-anomalies and a slight convex curvature towards HREE. However, sample 4HS is highest in Σ REY and also differs by having a negative Eu-anomaly and downwards-slope for the Yb–Lu segment (4HS, Fig. 14). Calcic skarn can also show distinct trends for titanites in the same sample, e.g., inversion of the Eu-anomaly for retrograde alteration (18HS-T2), LREE-poor, HREE-rich trends for titanite next to pyrite infilling fractured magnetite (10HS- and 11HS-T2; Fig. 14).

Importantly, titanite in ore-stage altered skarn shows distinct, concave trends (up-HREE) relative to calcic skarn, and positive Eu- and Y-anomalies.

Titanite contains a diverse range of other elements, including 2–3 wt.% (Al + Fe), Ta (hundreds of ppm), Nb and Zr (both up to thousands of ppm), Th (a few tens of ppm) and U (hundreds and sometimes, thousands of ppm). Arsenic attains concentrations of a few tens of ppm in skarn titanite and V reaches >500 ppm in prograde titanite.

Both titanite and allanite are excellent hosts for Sn and U. Fig. 8d shows a good correlation between the two elements in titanite across all lithologies, except in early-skarn and MW rocks which plot astray. Tin concentrations are up to 3000 ppm in main-stage calcic skarn. Uranium in titanite from early-skarn is as rich as in calcic skarn but much

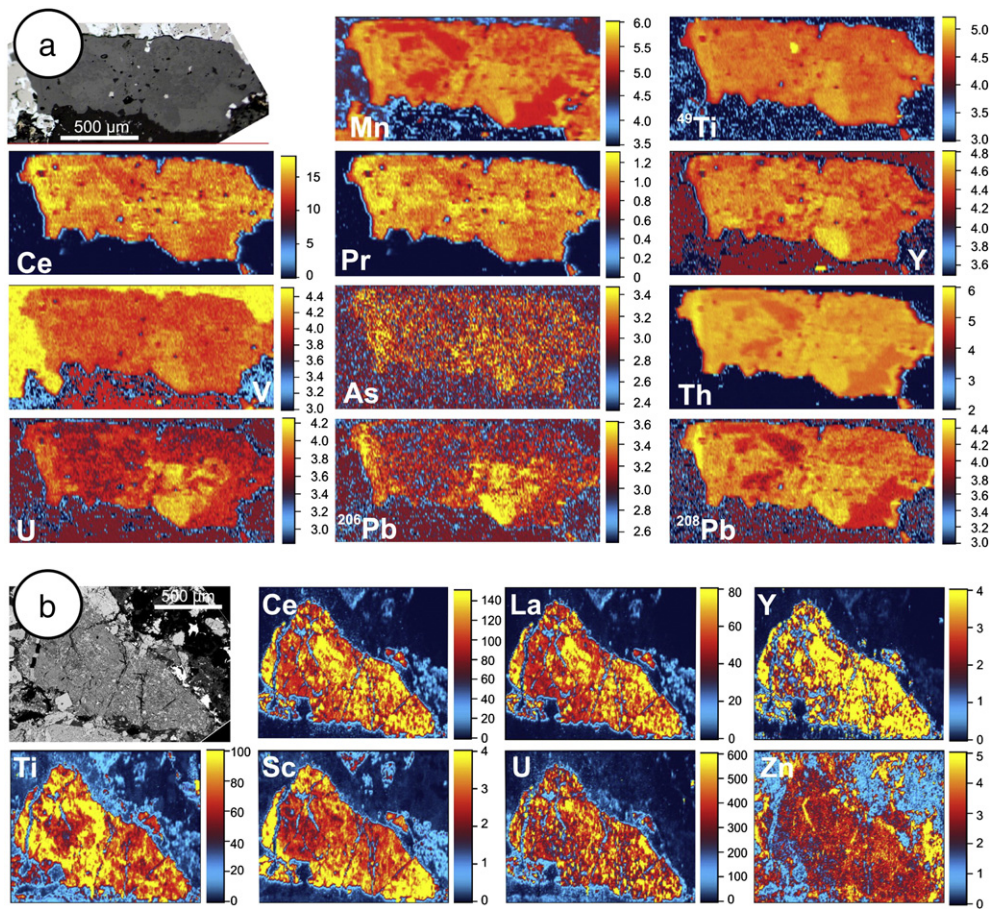


Fig. 15. LA-ICP-MS element maps for (a) zoned allanite (7HS) and (b) coarse, ore-stage allanite (5HS). On (a), scales in cps on a log-scale (10^0), except Ce (linear scale, cps $\times 10^6$). On (b), scales in cps on a linear-scale $\times 10^6$, except U ($\times 10^3$), Ti ($\times 10^4$) and Sc ($\times 10^5$).

lower in Sn. Both elements are surprisingly high in titanite from MW red-rock.

6.8. Apatite

Minerals of the apatite-supergroup can incorporate up to several wt.% $\sum \text{REE}$. Substitution of REE^{3+} for Ca^{2+} is compensated by replacement of P^{5+} by Si^{4+} . LA-ICP-MS spot analyses of apatite in 11 samples (Electronic Appendix C7, Fig. 14) shows that phosphate is strongly REE-enriched but with $\sum \text{REY}$ values ranging from 1100 ppm to >2 wt.%. Apatite from calcic skarn is characterized by consistent $\sum \text{REY}$ concentrations of 3000–7000 ppm. The highest $\sum \text{REY}$ concentrations are seen in Hillside granite, both in fresh and in ore-stage altered samples (26HS and 23HS, respectively).

Apatite from MW 'green-rock' II (17HS) shows pronounced decreasing LREE-to-HREE trends and positive Eu-anomaly. In contrast, MW 'red-rock', magmatic cores in granite, early skarn and calcic skarn have similar, relatively flat trends with a marked negative Eu-anomaly (Fig. 14). Rims in apatite from granite (hydrothermal overprint) are strongly LREE-enriched. Different trends in the same sample are seen in cases where apatite is embedded within sulfides typical of ore-stage initiation (5HS). In this case, the trend changes progressively from flat (T1) to up-HREE (T2), with increasingly positive Y-anomaly but no change in the Eu-anomaly. Similarly, pronounced HREE-enrichment is shown by apatite from ore-stage altered granite, where a positive Eu-anomaly occurs.

The dataset shows modest concentrations of Sr (at most a couple of hundred ppm), As (highest in main-stage calcic skarn), Zn, and varied

Th/U ratios (typically >1 in skarn apatite). Element mapping of apatite (not shown) confirms irregular grain-scale distribution of REE. Yttrium and HREE may display quasi-sectorial zoning and are often enriched towards the grain rim. HREE-rich sectors also contain markedly higher concentrations of U, Th and radiogenic Pb.

6.9. Geothermometry

The presence of titanite in almost all lithologies, and precise, ppm-level analysis of Zr in each, allow application of the Zr-in-titanite thermobarometer (Hayden et al., 2008). Measured concentrations of Zr in titanite from different rocks (Electronic Appendix C9, Fig. 16a), divided on the basis of their REE patterns, show decreasing concentrations from early albite–pyroxene, through main calcic skarn, to early ore-stage (chalcopyrite precipitation). Each sample shows a spread in absolute Zr concentration (Fig. 16a). Highest Zr concentrations are measured from early albite–pyroxene skarn (7HS), although comparable values are also recorded in one calcic skarn (4HS). We note that a consistent dataset is obtained for one calcic skarn sample (3HS): >70 spot analyses with a mean of 126 ppm Zr and small standard deviation (18 ppm), and also for 10HS (trend 1; 81 ± 30 ppm), characteristic of the early ore-stage. The lowest Zr concentrations are measured in retrogressed calcic skarn (a few ppm).

Considering the distribution of the skarn as narrow, patchy bodies at the contact between magmatic rocks and sedimentary protoliths (an attribute of deep skarns; e.g., Meinert et al., 2005), and the relatively deep setting of skarn-type IOCG systems (Williams et al., 2005) we estimate a formation depth of 7–10 km, corresponding to ~ 2 kbar.

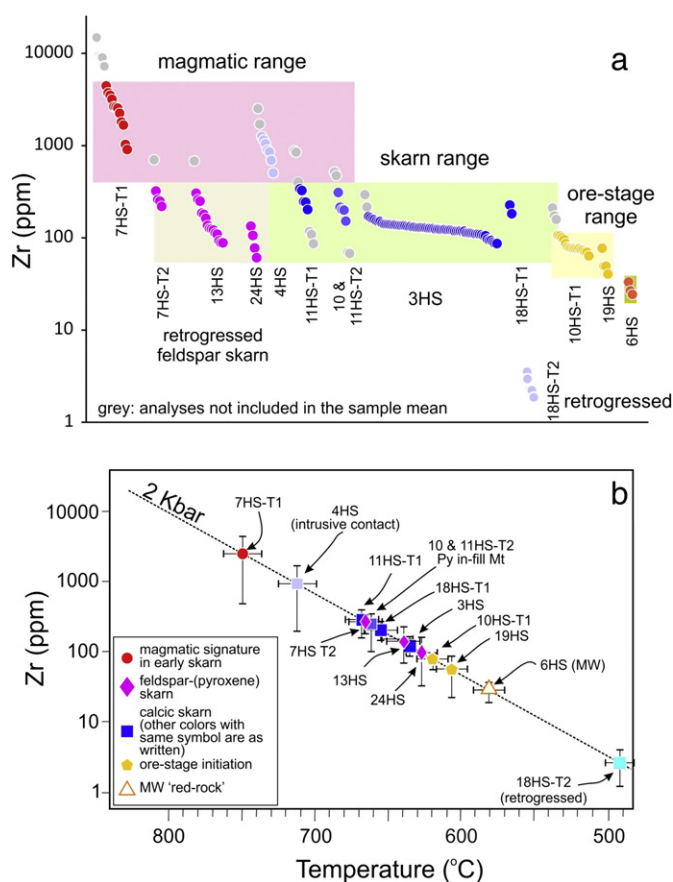


Fig. 16. (a) Cumulative frequency plot of Zr concentrations in titanite; sub-populations are divided according to classifications given in Fig. 14. (b) Temperature estimates from Zr-in-titanite geothermometry (calibration after Hayden et al., 2008). See text for explanation. Horizontal and vertical error bars on (b) represent 2σ error on calibration ($^{\circ}\text{C}$) and measured mean composition for Zr (ppm), respectively.

Calculated temperatures for each mean (Electronic Appendix C9) are plotted on the calibration curve of Hayden et al. (2008) at 2 kbar (Fig. 16b). Three temperature ranges are obtained: 750–670 $^{\circ}\text{C}$ for feldspar-dominant rocks, including early albite–pyroxene skarn; 720–625 $^{\circ}\text{C}$ for main calcic skarn; and 620–600 $^{\circ}\text{C}$ for the onset of the ore-stage (chalcopyrite precipitation). Titanite in the sample containing pyrite in-filled by magnetite falls within the temperature range of the main calcic skarn, drawing attention to the position of the pyrite–magnetite assemblage as clearly before the ore-stage. Titanite in the MW rocks gives temperatures of ~ 580 $^{\circ}\text{C}$.

These estimates are realistic in light of heat flow–balance constraints in contact thermal aureoles. Assuming an initial magma temperature (T_m) of 900 $^{\circ}\text{C}$, a depth of 7–10 km and a thermal gradient of 33 $^{\circ}\text{C}/\text{km}$, corresponding to an initial rock temperature (T_o) of 330–230 $^{\circ}\text{C}$, we apply the general equation of Bowman (1998), $T_c = 0.6(T_m - T_o) + T_o$. A maximum temperature in wallrock at the igneous contact (T_c) of 672–632 $^{\circ}\text{C}$ is obtained. Measured Ti in zircon from sample 7HS (359 ppm, EPMA data) gives a temperature of ~ 1197 $^{\circ}\text{C}$ applying the geothermometer of Watson et al. (2006), consistent with an early magmatic origin.

Temperature constraints during the late (calcite–quartz–chlorite) ore-stage are derived by application of geothermometry, based on the Al^{IV} (tetrahedral) component in chlorites (Cathelineau, 1988; De Caritat et al., 1993). Temperatures in the range of 311–201 $^{\circ}\text{C}$ are obtained using the calibrations of Cathelineau (1988) (Electronic Appendix Table B7).

7. Discussion

Skarn silicates and accessories play major roles in governing REY-trends at Hillside and can thus map the evolution of the mineralizing system. Although discrete REE-minerals are observed in the sample suite, their relative scarcity (except when allanite is present) suggests that they are only minor REY-carriers. Garnet is the major REY-host in the garnetite but a calculation for typical multi-component skarn (30% garnet, 30% clinozoisite, 15% pyroxene, 25% feldspar + quartz + calcite), using average REY concentrations in these minerals, shows that clinozoisite and garnet account for $>90\%$ of Σ REY.

7.1. Petrogenetic interpretation

The validity of REY trends as petrogenetic tools in magmatic processes relies on the chemistry of the trivalent REY controlled by the regular decrease in ionic radius with increasing atomic number. Hydrothermal processes can fractionate adjacent isovalent elements in the REE series from one another (e.g., Bau, 1991). Europium and Ce can change oxidation state from Eu^{3+} to Eu^{2+} , and Ce^{3+} to Ce^{4+} , giving either positive or negative anomalies on chondrite-normalized plots (Figs. 7, 9 and 12–14), which are quantifiable relative to neighboring elements. Yttrium does not change oxidation state but can show anomalous behavior relative to adjacent Ho in hydrothermal systems (Bau and Dulski, 1995). The Y-anomaly is thus a useful discriminant in magmatic-hydrothermal systems (Smith et al., 2009). Eu-, Ce- and Y-anomalies, $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{CN}}/[(\text{Sm}_{\text{CN}} + \text{Gd}_{\text{CN}})/2]$; $\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{CN}}/[(\text{La}_{\text{CN}} + \text{Pr}_{\text{CN}})/2]$, and $\text{Y}/\text{Y}^* = \text{Y}_{\text{CN}}/[(\text{Dy}_{\text{CN}} + \text{Ho}_{\text{CN}})/2]$, in individual minerals, as well as other ratios between different REE, are increasingly used for determining fluid sources and mineralization stages (e.g., Cao et al., 2012; Smith et al., 2004, 2009).

Eu/Eu^* vs. Ce/Ce^* (Fig. 17a) separates magmatic K-feldspar (granite), the MW red-rock protolith and hydrothermal feldspar. Granite K-feldspar fractionates both Eu and Ce showing the largest positive Eu-anomaly and largest negative Ce-anomaly. Variation in Eu/Eu^* and Ce/Ce^* in hydrothermal feldspar is consistent with varying oxidation states controlling fractionation during fluid–rock interaction, either modifying inherited trends from the protolith (8HS, 15HS), or formation of K-feldspar during the early- or late-stage. For example, K-feldspar in the latter has no Ce-anomaly but the largest positive Eu-anomaly among the hydrothermal feldspars, consistent with higher $f\text{O}_2$ (formation of late hematite). If validated on more samples, this framework can be used as a tool to recognize feldspar generations resulting from fluid–rock interaction in a context where inherited signatures correspond to more than one origin.

Variations in Y- and Eu-anomalies, and changes in REY-slopes, make accessory minerals ideal for tracking evolutionary trends throughout the entire lifespan of the system. The size and sense of Eu-, and possibly also Y-anomalies for titanite, apatite and allanite show distinct fields for defined lithologies and can be used to identify relative redox changes during evolution from the preserved magmatic signature in early-skarn to ore-stage (Fig. 17b, c).

Changes from LREE- to HREE-enrichment correlate with variation in Eu- and Y-anomalies from magmatic to ore-stage. This can be related to redox conditions evolving from magnetite- to hematite stability, and also involving $f\text{S}_2$ -shifts leading to sulfide precipitation. The relative positions of the clusters defining different lithologies and stages on Fig. 17 vary however. Apatite shows a flat trend in terms of Eu-anomaly (consistently ~ 0.5) from early- to ore-stage as HREE/LREE increases, whereas the Y-anomaly increases (from 1.2 to 2) over the same interval. In contrast, titanite shows a weak upwards-trend in terms of Eu-anomaly from the magmatic stage (0.5) to ~ 1 for most skarns. Ore-stage titanite stands out, however, by having Eu/Eu^* values of 0.75–2.5. There is no Y-anomaly in magmatic titanite but calcic and ore-stage titanite have ranges of positive Y-anomalies up to 1.4. On both plots, titanite from samples in which pyrite in-fills magnetite undergoing replacement by

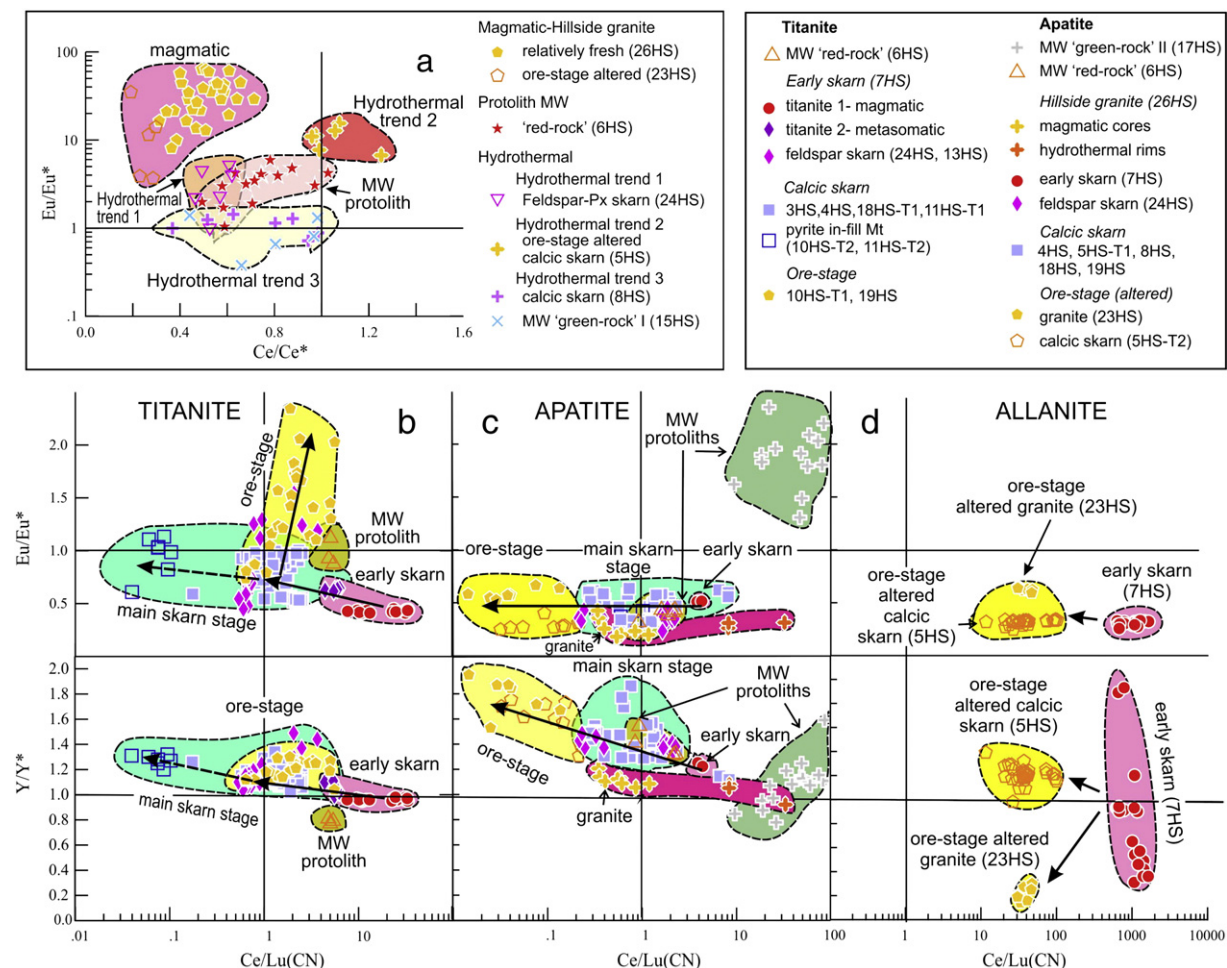


Fig. 17. (a) Eu/Eu^* vs. Ce/Ce^* for K-feldspar. (b–d) Eu/Eu^* and Y/Y^* vs. $(\text{Ce}/\text{Lu})_{\text{CN}}$ for titanite, apatite and allanite, respectively. Thick arrows show interpreted trends. See text for additional explanation.

hematite, is most strongly HREE-enriched, with slightly higher Y/Y^* than other skarns but no Eu/Eu^* anomaly. The likely explanation for the different behavior of apatite and titanite is preferential partitioning of Eu and Y since the two minerals co-crystallize, often as inclusions in one-another, especially when seen in skarn minerals.

Magmatic (core) apatite from granite overlaps with calcic skarn in terms of Eu/Eu^* but is discriminated from the skarn in terms of Y/Y^* (Fig. 17c). It shows a similar negative Eu-anomaly ($\text{Eu}/\text{Eu}^* < 0.4$) as apatite in moderately reduced I-type syenogranite with affiliated porphyry Mo–W and skarn deposits (Cao et al., 2012). In contrast, however, granite apatite at Hillside also displays a positive Ce-anomaly (not shown). Hydrothermal rims of apatite in the granite show much higher LREE/HREE. Apatite in MW green-rock shows distinct fields that do not overlap with skarn.

Magmatic allanite in early-skarn is discriminated from ore-stage allanite by higher LREE/HREE but not by Eu-anomaly, although ore-stage allanite in altered granite has higher Eu/Eu^* (Fig. 17d). A wide variation in Y/Y^* from magmatic allanite, consistent with the marked grain-scale zoning (Fig. 15a), is noted. Ore-stage allanite in altered granite defines a field with large negative Y-anomaly whereas ore-stage allanite in altered skarn has a modest positive Y-anomaly.

Fig. 18a separates prograde-proximal, prograde-distal and retrograde generations of skarn silicates, confirming changing LREE/HREE and redox conditions during skarn evolution. This is shown by positive Eu-anomalies for zoned garnet in calcic skarn, distal garnet and clinozoisite. All garnet, pyroxene and actinolite have $(\text{Ce}/\text{Lu})_{\text{CN}} < 1$ whereas clinozoisite has $(\text{Ce}/\text{Lu})_{\text{CN}} > 1$. Pyroxene in calcic skarn is HREE-enriched relative to pyroxene in early-skarn, and prograde garnet

in garnetite, and most calcic skarns are HREE-enriched relative to pyroxene. Retrograde and distal skarn minerals show greater spreads in Eu/Eu^* than prograde generations.

The Y/Y^* vs. $(\text{Ce}/\text{Lu})_{\text{CN}}$ diagram (Fig. 18b) discriminates prograde skarn minerals in different associations and stages more effectively than a plot of Eu/Eu^* vs. $(\text{Ce}/\text{Lu})_{\text{CN}}$. The apparent correlation between decreasing Y/Y^* with increase in $(\text{Ce}/\text{Lu})_{\text{CN}}$ in prograde garnet from garnetite reflects variation in one anomalously REY-rich sample (1HS), as much as the N-to-S change in the trace element endowment in garnet (Fig. 6). This may reflect an indirect response to redox conditions and/or relative proportions of different substitution mechanisms for Y-incorporation in garnet (see below). Garnet in multi-component calcic skarn has Y/Y^* of up to 1.5 but pyroxene in all lithologies displays a stronger positive Y-anomaly (Y/Y^* up to 3). Clinozoisite forming oscillatory bands with garnet in distal skarn has the highest positive anomaly ($\text{Y}/\text{Y}^* = 2.5\text{--}4.5$). The two generations of clinozoisite are clearly distinguishable in terms of Y/Y^* ($\text{Y}/\text{Y}^* = 1.2\text{--}2.5$ in proximal retrograde clinozoisite).

7.2. Towards a genetic model

Figs. 17 and 18 show that the REE signatures of accessory and skarn minerals record a change from HREE- to LREE-dominant over the lifespan of the system. REY patterns for the skarn minerals also clearly express the prograde to retrograde transition, as well as that from proximal to distal in calcic skarn. LREE/HREE evolution from early-skarn to ore-stage may have been accompanied by a $f\text{O}_2$ shift towards more

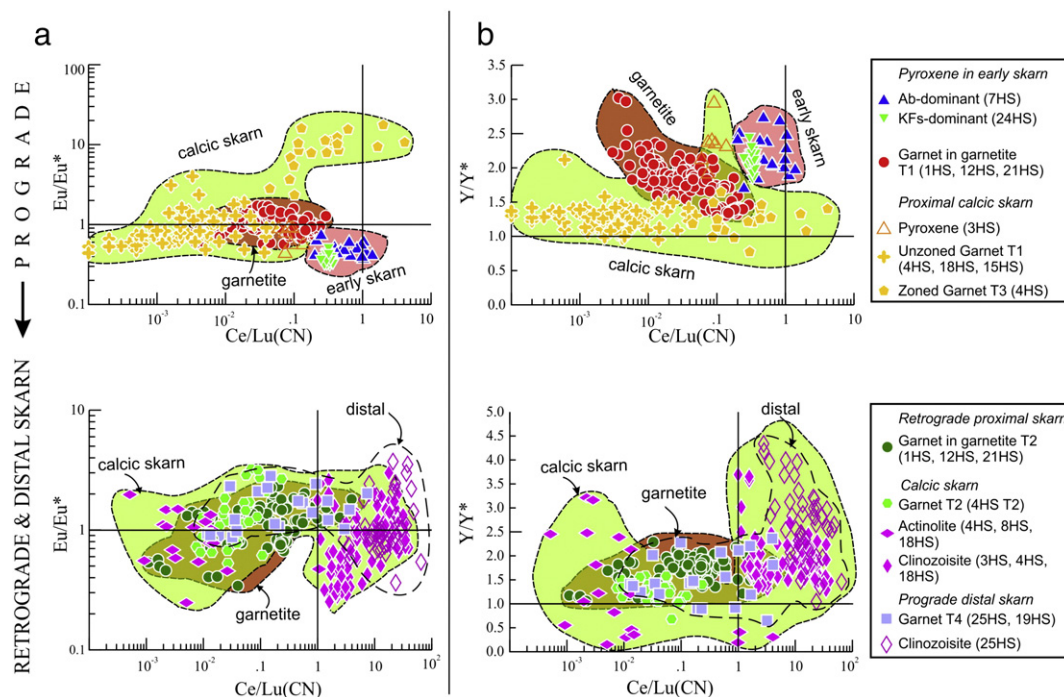


Fig. 18. (a) Eu/Eu^* and (b) Y/Y^* vs. $(\text{Ce}/\text{Lu})_{\text{CN}}$ for skarn assemblages. See text for explanation.

oxidizing conditions (hematite stability); $f\text{S}_2$ also likely increased over the same stages. Accessories are particularly sensitive to $f\text{S}_2$ increase.

The present data, although limited, is useful for constraining a genetic model for mineralization. An important question for Hillside is to pinpoint differences between metasomatism associated with regional metamorphism (formation of calc-silicate-feldspar-bearing rocks such as the MW sequences), and skarn alteration *sensu stricto*, i.e., relating to contact aureoles of magmatic intrusions. This would allow a better understanding of protolith constraints on skarn formation, as well as clarifying whether MW metasomatism (considered coeval with Hiltaba magmatism by [Conor et al., 2010](#)), is part of the broad, regional-scale IOCG alteration, or alternatively, has a distinct geochemical character resulting from fluid–rock interaction involving different fluid sources.

Outcomes here highlight several issues (e.g., REY and LILE signatures in K-feldspar, calc-silicates and accessories) that could be pursued in a regional-scale approach to resolve the above question. Overall, the lower REY content in clinzoisite and Zr in titanite, the strong contrast between apatite from ‘red’ and ‘green’ MW rocks, as well as the surprisingly high U/Th ratios in feldspar, indicate that the geochemical expression of metasomatism in the MW rocks is different to that in skarn associated with Hiltaba Suite intrusions. A more consistent sample suite is however necessary to quantify the nature of this difference.

Similar to the findings here, LREE-enrichment in both titanite and allanite from Kirunavaara, Sweden, was linked by [Smith et al. \(2009\)](#) to a granitic source, contrasting with a population of HREE-enriched titanite linked to leaching of metals from host mafic volcanics. [Smith et al. \(2009\)](#) note HFSE-enrichment across their dataset, a feature interpreted in terms of either highly saline, high-F fluids, or both. A significant difference between the Hillside and Kirunavaara datasets is, however, the consistently high U/Th ratio in Hillside titanite. This discrepancy could be due to different geological settings but could be an argument favoring leaching of metals from U- and REE-rich lithologies in the MW Group.

7.2.1. Magmatic to early-skarn stage

The distinct geochemical character of early feldspar–pyroxene skarn is seen in [Figs. 17 and 18](#). Mineral trace element signatures support the presence of both preserved magmatic and overprinting hydrothermal

components in this rock, as inferred from petrography. Pyroxene in some early skarn is Cr–Ni-richer ([Fig. 8c](#)), also supporting preservation of inherited magmatic signatures into the hydrothermal stage. Accordingly, we interpret the early skarn as the product of fluid–rock interaction evolving from rock- to fluid-buffered.

Pyroxene and albite can be tied to the early transition from magmatic to metasomatic regimes whereby the latter evolves further into retrograde formation of K-feldspar and hematite. REY plots for accessories tied to the metasomatic stage in feldspar-dominated skarn show characteristics shared with calcic skarn ([Fig. 17](#)).

Early-skarn stage, bracketed between $\sim 750^\circ\text{C}$ (high-Zr titanite, Ttn-1) and $670\text{--}630^\circ\text{C}$ (Ttn-2 and other feldspar-skarn samples), is characterized by LREE-enrichment in pyroxene and accessories relative to calcic skarn. Feldspar-dominated alteration points at an early albitization followed by K-feldspar alteration in an IOCG system ([Williams et al., 2005](#)).

7.2.2. Main skarn stage

The similar temperatures estimated from Zr-in-titanite geothermometry in feldspar-rich rocks and prograde calcic skarn ($670\text{--}630^\circ\text{C}$) infer immediate intrusive contacts in both cases but formation on behalf of different protoliths, i.e., magmatic and feldspar-bearing MW carbonate/calc-silicate rocks, respectively. Higher Zr-contents in titanite, falling into the magmatic range but with fractionation trends similar to calcic skarn titanite ([Fig. 14](#)) suggest erratic fragmentation and enclosure of MW rocks within magmatic rocks at the end of their crystallization leading to high-T hornfels reactions prior to metasomatism. Such titanite would retain this early signature since temperatures are below titanite resetting (e.g., [Frost et al., 2000](#)) and no evidence for dissolution–reprecipitation overprint is observed (e.g., 4HS). Skarn undergoing pronounced retrograde alteration is characterized by lower temperatures ($\sim 490^\circ\text{C}$) estimated from titanite displaying distinct fractionation trends (18HS-T2; [Fig. 14](#)) and formed where actinolite replaces pyroxene (18HS). Titanite within magnetite from this sample, displays however the typical prograde trends ([Fig. 14](#)).

Prograde skarn is defined by a general lack of Fe/Al zoning in garnet, inferring rapid growth via infiltration leading to a fluid-buffered REY-signature. The REE pattern of fluid is governed by complexation

processes causing HREE-dominant trends at 600 °C and near-neutral to mildly-basic environments (Bau, 1991). Such conditions are feasible for Hillside skarn (magnetite-stable) and thus explain the prevalent HREE-dominant character of this fluid (shown by both garnet and pyroxene in Fig. 17). Fluid pH remains neutral throughout skarn formation (late adularia reported; Connor et al., 2010) but redox state increases as hematite gradually replaces magnetite. The consistent change from HREE- to LREE-dominant trends in both retrograde garnet and clinozoisite may relate to a change from high- to low-salinity fluids (typical for both skarn and IOCG systems (e.g., Meinert et al., 2005; Williams et al., 2005)).

Skarn garnet has been the focus of several studies comprising both analytical and numerical modeling. Gaspar et al. (2008) and Smith et al. (2004) indicate that Fe- and Al-zoning in garnet supports strong partitioning between LREE to HREE via an intracrystalline effect, i.e., where Fe- and Al-rich zones are preferentially enriched in LREE and HREE, respectively, and where the main substitution is YAG-type. In contrast, unzoned garnet at Hillside (~And₇₀Gr₃₀), consistently concentrates HREE relative to LREE (Ce/Lu < 1; Fig. 18). The alternative, 'menzerite-type' substitution mechanism for REY-incorporation involving Fe²⁺ advanced by Carlson (2012) and Grew et al. (2010), could explain the anomalously high Y + (H)REE incorporation in garnetite (up to 25,000 ppm, where Y = 19,000 ppm) and hint at the importance of redox processes.

Prograde garnet, although rarely zoned with respect to major components, is always characterized by zonation with respect to REY, incompatible, and other trace elements (Fig. 10); repeated fluid infiltration in parts of the system can be inferred from superpositioning of zonation patterns (Fig. 11). Such differential behavior can be explained by variable kinetics of garnet growth with respect to major components relative to minor/trace elements as indicated by numerical modeling of diffusional mechanisms for a range of different elements (Carlson, 2012).

The role of Al-for-Fe (YAG-type) substitution as a driver of REY incorporation into Hillside garnet only appears significant in local closed-system conditions (retrograde (re)-crystallization), in an otherwise open-system (co-existence of zoned and unzoned garnet). The strong decoupling of Eu from other REE in Fe-rich zoned garnet (T3; Fig. 9), analogous to garnets from the Beinn Dubhaich contact aureole, Scotland (Smith et al., 2004), relates only to such diffusion-driven, closed-systems at Hillside.

Migdisov et al. (2009) show that, in a hydrothermal fluid, REE transport is facilitated by formation of chloride, fluoride, and hydroxide complexes at acidic, neutral, and basic pH conditions, respectively. HREE are complexed by fluoride, and less by chloride than LREE, whereas at basic pH conditions, HREE and LREE associate with hydroxide to an equivalent degree. Chloride-complexes are typically of skarn fluids (e.g., Meinert et al., 2005) but fluoride ligands (also enhancing HFSE solubility) are considered critical for transport of U- and REE-complexes in IOCG deposits of the Olympic Province (e.g., McPhie et al., 2011). Although all skarn minerals and accessories contain measurable F (Electronic Appendix B), fluorite is extremely rare at Hillside unlike other deposits in the province. This leaves the question of REE- and U-complexation open, but points to substantially different fluid characters in giant, sericite-altered, hematite-dominant IOCG systems, and deeper, skarn-style deposits. Fluid inclusion studies would help validate these interpretations.

7.2.3. Ore-stage

The ore-stage, bracketed between 620–600 °C (Zr-in-titanite) and 300–200 °C (chlorite geothermometry), is defined by distinct fractionation trends in all accessories (Figs. 14 and 17b–d). As previously recognized for ore-stage allanite at Hillside (Gregory et al., 2011), our dataset shows that titanite and apatite also have HREE-enriched fractionation trends in samples where this alteration is prominent. The marked Sn and U signature of Hillside skarn, with concentrations highest in

ore-stage accessory minerals but also present in garnetite indicates a granitic affiliation and an early introduction of these elements into the system.

7.3. Exploration significance

Variation in trace element signatures and chondrite-normalized diagrams for individual minerals shows that skarn-type IOCG deposits have distinct signatures applicable to exploration. A successful exploration model would, however, depend on: the widespread presence of the same mineral in proximal, distal and regional alteration; measurable concentrations of the elements of interest; and systematic compositional variation between spatially- or genetically-definable populations. The presence of calc-silicates or apatite with distinct REY patterns, or enrichment in key elements, could, for example, be indicative of position within an IOCG system and whether this is Cu–Au-bearing or barren. A fuller discussion of the exploration significance is beyond the scope of the present study. This would require a more comprehensive study of mineral geochemistry at the margins of the system, both laterally and vertically. Requisite sample material for such a study at Hillside is not yet available.

8. Conclusions

- REY and incompatible element signatures of minerals are geochemical tracers for alteration patterns from magmatic- to ore-stages in IOCG-skarn systems.
- REY patterns in co-existing minerals allow for assessment of the relative roles played by magmatic and hydrothermal processes, the change in fluid parameters during skarn evolution, and the importance of fluid salinity in stabilizing REY-complexes in fluid.
- A redox shift towards higher fO_2 – fS_2 at 620–200 °C during the ore-stage depicts a marked but variable increase in HREE-fractionation into titanite, apatite and allanite. These trends could be used to distinguish mineralized from non-mineralized IOCG systems.
- Titanite and apatite show particular promise because of their characteristically distinct REY patterns in magmatic and hydrothermal environments, good response to redox changes and abundance throughout different lithologies.

Acknowledgments

We gratefully acknowledge Rex Minerals for approval to publish these results and Marc Twining for guidance and discussion, DET CRC for funding, and Adelaide Microscopy for analytical support. We thank two anonymous reviewers for helpful comments. This is TRaX contribution 269.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2013.07.023>.

References

- Bau, M., 1991. Rare earth element mobility during hydrothermal and metamorphic fluid–rock interaction and the significance of the oxidation state of europium. *Chemical Geology* 93, 219–230.
- Bau, M., Dulski, P., 1995. Comparative study of yttrium and rare-earth element behaviours in fluorine-rich hydrothermal fluids. *Contributions to Mineralogy and Petrology* 119 (213), 223.
- Bau, M., 1996. Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology* 123, 323–333.
- Bea, F., 1996. Residence of REE, Y, Th and U in granites and crustal protoliths: implications for the chemistry of crustal melts. *Journal of Petrology* 37, 521–552.
- Bottazzi, P., Tiepolo, M., Vannucci, R., Zanetti, A., Brumm, R., Foley, S.F., Obertli, R., 1999. Distinct site preferences for heavy and light REE in amphibole and

- the prediction of $\text{Amph/LD}_{\text{REE}}$. *Contributions to Mineralogy and Petrology* 137, 36–45.
- Bowman, J.R., 1998. Basic aspects and applications of phase equilibria in the analysis of metasomatic Ca–Mg–Al–Fe–Si skarns. In: Lentz, D.R. (Ed.), *Mineralised Intrusion-related Skarn Systems*. Mineralogical Association of Canada Short Course, vol. 26, pp. 1–49.
- Cao, M., Li, G., Qin, K., Seitmuratova, E.Y., Liu, Y., 2012. Major and trace element characteristics of apatites in granitoids from Central Kazakhstan: implications for petrogenesis and mineralization. *Resource Geology* 62, 63–83.
- Carlson, W.D., 2012. Rates and mechanism of Y, REE, and Cr diffusion in garnet. *American Mineralogist* 97, 1598–1618.
- Cathelineau, M., 1988. Cation site occupancy in chlorites and illites as a function of temperature. *Clays and Clay Minerals* 23, 471–485.
- Cherniak, D.J., 1998. REE diffusion in calcite. *Earth and Planetary Science Letters* 160, 273–287.
- Ciobanu, C.L., Wade, B.P., Cook, N.J., Schmidt Mumm, A., Giles, D., 2013. Uranium-bearing hematite from the Olympic Dam Cu–U–Au deposit, South Australia; a geochemical tracer and reconnaissance Pb–Pb geochronometer. *Precambrian Research* 238, 129–147. <http://dx.doi.org/10.1016/j.precamres.2013.10.007>.
- Conor, C., Raymond, O., Baker, T., Teale, G., Say, P., Lowe, G., 2010. Alteration and mineralisation in the Moonta–Wallaroo Cu–Au mining field region, Olympic Domain, South Australia. In: Porter, T.M. (Ed.), *Hydrothermal Iron Oxide Copper–Gold and Related Deposits: A Global Perspective*, vols. 3 and 4. PGC Publishing, Adelaide, pp. 1–24.
- De Caritat, T.P., Hutcheon, I., Walshe, J.L., 1993. Chlorite geothermometry: a review. *Clays and Clay Minerals* 41, 219–239.
- Enami, M., Cong, B., Yoshida, H., Kawabe, I., 1995. A mechanism for Na incorporation in garnet: an example from garnet in orthogneiss from the Su–Lu terrane, eastern China. *American Mineralogist* 80, 475–482.
- Frei, D., Liebscher, A., Franz, G., Dulski, P., 2004. Trace element geochemistry of epidote minerals. *Reviews in Mineralogy and Geochemistry* 56, 553–605.
- Frost, B.R., Chamberlain, K.R., Schumacher, J.C., 2000. Sphene (titanite): phase relations and role as a geochronometer. *Chemical Geology* 172, 131–148.
- Gaspar, M., Knaack, C., Meinert, L.D., Moretti, R., 2008. REE in skarn systems: a LA-ICP-MS study of garnets from the Crown Jewel gold deposit. *Geochimica et Cosmochimica Acta* 72, 185–205.
- Gieré, R., Sorensen, S.S., 2004. Allanite and other REE-rich epidote-group minerals. *Reviews in Mineralogy and Geochemistry* 56, 431–493.
- Gregory, C.J., Reid, A.J., Say, P., Teale, G.S., 2011. U–Pb geochronology of hydrothermal allanite and titanite and magmatic zircon from the Hillside Cu–Au deposit, Yorke Peninsula. In: Reid, A.J., Jagodzinski, E.A. (Eds.), *PACE Geochronology: Results of Collaborative Geochronology Projects 2009–10 South Australia*. Department of Primary Industries and Resources, pp. 95–126 (Report Book 2011/00003).
- Grew, E.S., Marsh, J.H., Yates, M.G., Lazic, B., Armbruster, T., Locock, A., Bell, S.W., Dyar, M.D., Bernhardt, H.-J., Medenbach, O., 2010. Menzerite-(Y), a new species, $\{(Y, \text{REE})(\text{Ca}, \text{Fe}^{2+})_2\}[(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})](\text{Si}_3)\text{O}_{12}$, from a felsic granulite, Parry Sound, Ontario, and a new garnet end-member, $\{\text{Y}_2\text{Ca}\}[\text{Mg}_2](\text{Si}_3)\text{O}_{12}$. *Canadian Mineralogist* 48, 1171–1193.
- Gromet, L.P., Silver, L.T., 1983. Rare earth element distributions among minerals in a granodiorite and their petrogenetic implications. *Geochimica et Cosmochimica Acta* 47, 925–939.
- Hand, M., Reid, A., Jagodzinski, E., 2007. Tectonic framework and evolution of the Gawler craton, South Australia. *Economic Geology* 102, 1377–1395.
- Hayden, L.A., Watson, E.B., Wark, D.A., 2008. A thermobarometer for sphene (titanite). *Contributions to Mineralogy and Petrology* 155, 529–540.
- Hayward, N., Skirrow, R.G., 2010. Geodynamic setting and controls on iron oxide Cu–Au ($\pm$ U) ore in the Gawler Craton, South Australia. In: Porter, T.M. (Ed.), *Hydrothermal Iron Oxide Copper–Gold and Related Deposits: A Global Perspective*, Vol. 3. PGC Publishing, Adelaide, pp. 1–27.
- Hitzman, M.W., 2000. Iron oxide–Cu–Au deposit: what, where, when, and why. In: Porter, T.M. (Ed.), *Hydrothermal Iron Oxide Copper–Gold and Related Deposits: A Global Perspective*. Australian Mineral Foundation, Adelaide, pp. 9–26.
- Jaffe, H.W., 1951. The role of yttrium and other minor elements in the garnet group. *American Mineralogist* 36, 133–155.
- McDonough, W.F., Sun, S.-s., 1995. The composition of the Earth. *Chemical Geology* 120, 223–253.
- McPhie, J., Kamenetsky, V.S., Allen, S., Ehrig, K., Agangi, A., Bath, A., 2011. The fluorine link between a supergiant ore deposit and a silicic large igneous province. *Geology* 39, 1003–1006.
- Meinert, L.D., Dipple, G.M., Nicolescu, S., 2005. World Skarn Deposits: Economic Geology 100th Anniversary Volume. 299–336.
- Migdisov, A.A., Williams-Jones, A.E., Wagner, T., 2009. An experimental study of the solubility and speciation of the Rare Earth Elements (III) in fluoride- and chloride-bearing aqueous solutions at temperatures up to 300 °C. *Geochimica et Cosmochimica Acta* 73, 7087–7109.
- Mulrooney, D., Rivers, T., 2005. Distribution of the rare-earth elements among coexisting minerals in metamorphic rocks across the epidote-out isograd: an example from the St. Anthony Complex, Northern Newfoundland, Canada. *Canadian Mineralogist* 43, 263–294.
- Rex Minerals, 2012. Annual report 2012. 72 pp. <http://www.rexminerals.com.au>.
- Skirrow, R.G., Bastrakov, E.N., Barovich, K., Fraser, G.L., Creaser, R., Fanning, M.C., Raymond, O.L., Davidson, G.J., 2007. Timing of iron oxide Cu–Au–(U) hydrothermal activity and Nd isotope constraints on metal sources in the Gawler craton, South Australia. *Economic Geology* 102, 1441–1470.
- Smith, M.P., Henderson, P., Jeffries, T.E.R., Long, J., Williams, C.T., 2004. The rare earth elements and uranium in garnets from the Beinn Dubhaich Aureole, Skye, Scotland, UK: constraints on processes in a dynamic hydrothermal system. *Journal of Petrology* 45, 457–484.
- Smith, M.P., Storey, C.D., Jeffries, T.E., Ryan, C., 2009. In situ U–Pb and trace element analysis of accessory minerals in the Kiruna District, Norrbotten, Sweden: new constraints on the timing and origin of mineralization. *Journal of Petrology* 50, 2063–2094.
- Tiepolo, M., Oberti, R., Vannucci, R., 2002. Trace-element incorporation in titanite: constraints from experimentally determined solid/liquid partition coefficients. *Chemical Geology* 191, 105–119.
- van Orman, J.A., Grove, T.L., Shimizu, N., 2001. Rare earth element diffusion in diopside: influence of temperature, pressure, and ionic radius and an elastic model for diffusion in silicates. *Contributions to Mineralogy and Petrology* 141, 687–703.
- Watson, E.B., Wark, D.A., Thomas, J.B., 2006. Crystallization thermometers for zircon and rutile. *Contributions to Mineralogy and Petrology* 151, 413–433.
- Williams, P.J., Barton, M.D., Johnson, D.A., Fontboté, L., de Haller, A., Mark, G., Oliver, N.H.S., Marschik, R., 2005. Iron oxide copper–gold deposits: geology, space–time distribution, and possible modes of origin. *Economic Geology* 100th Anniversary Volume, pp. 371–405.