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The occurrence of coarse-grained massive tilleyite in the Redcap Creek magmatic skarn, North Queensland

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ABSTRACT. Endoskarns formed where a swarm of diorite dykes have intruded calcite marble at Redcap Creek include an inner melilite-dominated, a wollastonite-dominated, and an outer massive tilleyite zone in contact with marble. The massive tilleyite is unusual in that it is coarse-grained (prisms 2–15 cm in length) and its deep grey colour contrasts with the lighter coloured varieties described elsewhere. A chemical analysis gives a formula close to ideal, with only minor substitution of Al, Ti, and Mg. Refined unit cell parameters are in close agreement with those quoted in the literature. The skarns have clearly formed by transport of Si, Mg, Fe, Al, and Ti from the igneous rocks, and Ca in the reverse direction from the marble. Activity diagrams derived from experimental data are most useful in interpreting the zonal sequence of endoskarns, and preliminary results suggest mass transfer at low X_{CO_2} and temperature of the order of 800 °C or higher for the formation of the massive tilleyite.

KEYWORDS: tilleyite, magmatic skarn, Redcap Creek, Queensland.

THE Chillagoe region in North Queensland is well known for abundant ore-bearing skarns containing sulphides, gold or cassiterite formed at or near the contacts of Carboniferous granitoids and Silurian limestones of the Chillagoe Formation (de Keyser and Wolff, 1964; Paverd, 1972, 1981). However, the tilleyite-bearing skarn, superbly exposed in Redcap Creek and the steep ridge on the eastern bank, is a non-mineralized magmatic skarn, formed by mass transfer between diorite dykes and marble which they have intruded. This skarn is situated about 300 km east of the city of Cairns, and 15 km north of the town of Chillagoe, from which it is accessible via a gravel road and bush tracks.

Skarn nomenclature used here is largely after Kerrick (1977) and Burt (1977), who refer to 'magmatic' skarns, formed at the igneous–marble contact, as distinct from 'vein' skarns which form along fractures in the marble. Magmatic skarns are subdivided into 'endoskarn' which has replaced igneous rock and 'exoskarn' which has replaced marble.

Geology of the magmatic skarn. Fig. 1 shows the Redcap Creek magmatic skarn situated at the southern margin of a Carboniferous granodiorite pluton, which has intruded the Silurian Chillagoe Formation, the Siluro-Devonian Mount Garnet Formation, and acid volcanics of probable Carboniferous age. Contrary to the interpretations of Paverd (1972, 1981), the magmatic skarn at Redcap Creek has not formed by reaction between the granodiorite and Chillagoe Formation marble, but instead by reaction between a diorite dyke swarm and marble. Abundant xenoliths of diorite, some up

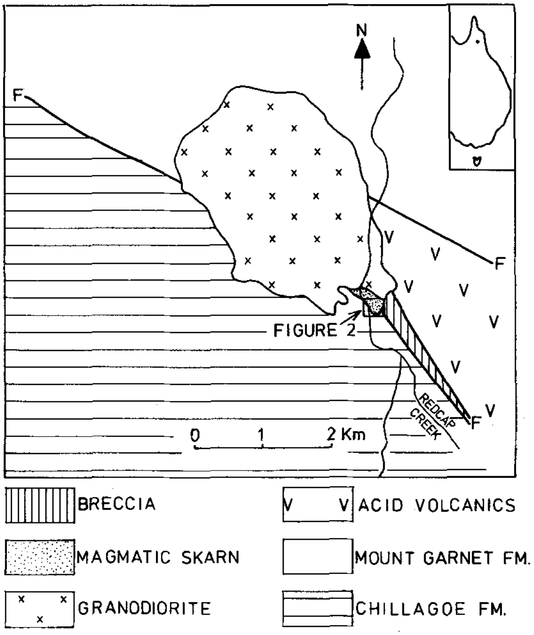

FIG. 1. Locality map for Redcap Creek magmatic skarn. The inset shows the location of the Redcap area in north Queensland, and the location of fig. 2 is indicated.

to 30 m in length, occur in the granodiorite immediately adjacent to the magmatic skarn. The shapes of the xenoliths, and in particular the abundant net veining of granodiorite in the diorite xenoliths, strongly suggests that magma mixing has taken place (Blake *et al.*, 1965). Elsewhere in the Chillagoe region, similar diorite dykes and xenoliths are described by Richards (1981), who suggests that they are genetically related to the granodiorite hosts. Despite such a likely genetic connection, the magmatic skarn at Redcap Creek has formed only at diorite-marble contacts, and no skarn development is present along the granodiorite-marble contact which was mapped in detail for a kilometre on the western side of the magmatic skarn.

The granodiorite is comprised of plagioclase, quartz, orthoclase, hornblende, and biotite. The diorite dykes are composed of the same minerals, but with a higher colour index, and little to no quartz or orthoclase. Augite occurs in some diorite specimens. The diorite dykes are commonly irregular in shape, but generally terminate as tongues in the marble. On the western side of the skarn in fig. 2, individual dykes of S, SW, WNW, and NNW orientations are present, and the general impression is of a crude radical pattern approximately centred in the middle of the skarn.

The diorite dykes have been variably replaced by endoskarn, while screens, tongues, and lenses of marble between the dykes, and to a limited extent marble rimming the outer dykes, have been replaced by a variety of exoskarns. The endoskarn is composed mainly of grossularite-andradite, with varying amounts of clinopyroxene (diopside or

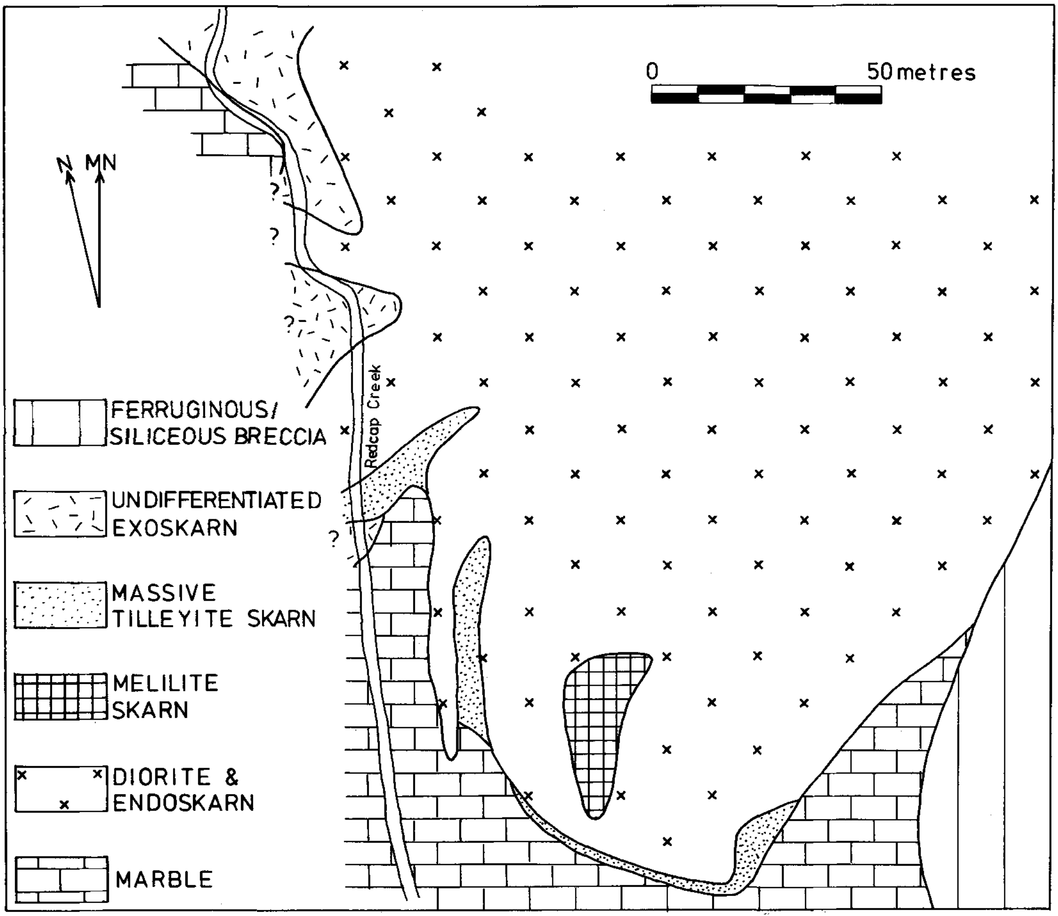

FIG. 2. Map of the southern part of the Redcap Creek magmatic skarn. Alluvium covers much of the bedrock west of the creek on this map. Only one larger lens of melilite skarn is shown, but numerous smaller lenses of melilite and other exoskarn types occur throughout the area labelled as diorite/endoskarn.

salite), with or without wollastonite, clinozoisite-epidote, and idocrase. In many places, unaltered diorite is left as pods or lenses within the endoskarn, commonly surrounded by concentric layers of varying mineralogy.

In the inner part of the skarn, the marble between the dykes has been totally replaced by exoskarn composed of granoblastic melilite containing some grossularite-andradite with variable TiO_2 content. At one outcrop a tilleyite-bearing layer occurs in melilite skarn. The outer exoskarn lenses, tongues, or rims are dominated by coarse-grained wollastonite, with or without calcite, idocrase, and grossularite-andradite (commonly TiO_2-rich). The coarse-grained massive tilleyite exoskarn is restricted to the southern extremity of the skarn (fig. 2).

The ferruginous-siliceous breccia which extends southwest of the magmatic skarn along a fault zone, is the surface expression of sulphide-bearing vein skarns, which probably formed at lower temperatures and later than the magmatic skarn (Paverd, 1972, 1981).

Tilleyite skarn. The coarse-grained massive tilleyite exoskarn (fig. 2) has a very sharp contact with marble on one side, while on the other it is separated from diorite/endoskarn by a zone 0.5-1 m wide of coarse wollastonite exoskarn containing garnet and vesuvianite. Tilleyite occurs as prismatic to tabular deep-grey crystals, commonly in the grainsize range 2-15 cm and weathering to white on outcrops (fig. 3). The crystals appear to be randomly oriented, but in places radiate outwards from small relict pods of marble. The massive tilleyite has been variably veined and replaced by the assemblage wollastonite-idocrase-melanite-garnet-calcite, the wollastonite being fibrous and finer-grained in comparison with the coarse prismatic grains in the adjacent wollastonite-dominated exoskarns.

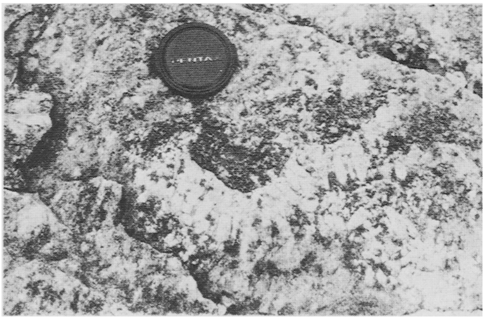

FIG. 3. Coarse prisms of tilleyite (light colour partly on weathered surface) replaced by idocrase, wollastonite, and garnet (dark).

Besides the coarse-grained massive tilleyite, this mineral has been found in only two other localities in the Redcap Creek skarn. One of these is a single layer within a melilite skarn (specimen RD11), which contains 3 mm oikocrysts of tilleyite with melilite, calcite, and garnet inclusions (analysis 2, Table I). The other sample, collected from the north-east edge of the skarn within 1 m of the granodiorite contact, consists of fine-grained tilleyite, calcite, garnet, and diopside.

Chemistry of tilleyite. The massive tilleyite analysis given in Table I conforms well with the accepted formula of $Ca_5Si_2O_7(CO_3)_2$. Very minor substitution of other elements occurs, the most significant being Ti for Si and Mg for Ca in specimen RG3. The original analysis from Crestmore (Larsen and Dunham, 1933) was contaminated with small amounts of other phases, as were the samples from Carlingford (Nockolds, 1947).

TABLE I. *Tilleyite analyses*

	1	2	3	4
SiO_2	23.70	23.55	24.1	24.48
TiO_2	0.11	0.05	—	—
Al_2O_3	0.02	0.00	0.0	0.42
FeO	0.01	0.08	0.0	0.40*
MnO	0.01	0.05	0.0	—
MgO	0.05	0.03	0.0	—
CaO	57.08	56.62	56.0	55.51
Na_2O	0.01	0.01	—	—
K_2O	0.00	0.01	—	—
CO_2	17.85	—	(18.0)	19.07
H_2O+	0.15	—	—	1.26
H_2O-	0.03	—	—	0.30
Total	99.02		98.1	100.44
Formula based on 13 oxygens				
Si	1.924			
Ti	0.090			
Al	0.002			
Fe	—			
Mn	—			
Mg	0.006			
Ca	4.965			
Na	0.002			
CO_2	1.979			
OH	0.081			

1. Tilleyite, massive coarse-grained, specimen RG3, Redcap Creek.
2. Tilleyite from layered melilite-tilleyite-garnet-calcite skarn, specimen RD11, Redcap Creek.
3. Microprobe analysis of tilleyite from Akagane Mine (Bunno *et al.*, 1982).
4. Tilleyite from Carlingford (Nockolds, 1947). *Fe in this sample is given as Fe_2O_3.

The specimens from Redcap Creek were analysed using a JXA-5A microprobe at the University of Melbourne.

The analysis for the Akagene Mine (Bunno *et al.*, 1982) is a partial miroprobe analysis, but shows no substitution. Note that the H_2O content of the Redcap sample is very small.

The deep-grey colour (slightly bluish) of the massive tilleyite is possibly due to the small TiO_2 content (0.11 %). A less likely possibility is the presence of abundant gas-filled tubules less than 10 μm in diameter.

X-ray diffraction studies. The partially indexed pattern, obtained by comparison with J.C.P.D.S. and Bunno *et al.* (1982), was then used to calculate unit cell parameters by a method of least squares refinement of $1/d^2$ values. From these parameters the peak positions and Miller indices appropriate to the monoclinic space group $P2_1/a$ were generated for FeKα up to 160° 2θ. The entire indexed pattern was subjected to a further least-squares refinement of cell parameters with a greater empirical weighting given to reflections of 2θ greater than 60°.

The refinement unit cell parameters and standard errors obtained in this study of tilleyite from Redcap Creek are given in Table II. These parameters are in close agreement with those quoted for natural specimens of tilleyite from Barnavave, Carlingford, Ireland, and Crestmore, California, USA (Louisnathan and Smith, 1970).

All reflections in the pattern could be indexed on the monoclinic space group $P2_1/a$ (Smith, 1953; Louisnathan and Smith, 1970).

Discussion. The lenses of massive tilleyite skarn at Redcap Creek are unusual tilleyite. (The wollastonite-garnet-idocrase assemblage formed later, veining and replacing the tilleyite.) In the descriptions from the classic localities in the US and the British Isles, tilleyite is typically fine-grained, white or light bluish-grey, and coexists with a variety of other minerals (Larsen and Dunham, 1933; Tilley, 1947; Nockolds, 1947; Burnham, 1959; Joesten, 1974). However, the Redcap Creek skarn has much in common with that described from the Sakae Adit, Akagene Mine in Japan, where a gabbro is followed successively by garnet skarn, vesuvianite skarn, gehlenite skarn (replaced by bicchulite), wollastonite-garnet skarn, massive tilleyite skarn (partly replaced by foshagite and calcite), and with a narrow spurrite layer in contact with marble (Bunno *et al.*, 1982). The Akagene tilleyite is also coarse (up to 25 cm in grain size), but generally light brown to cream in colour.

The Redcap Creek magmatic skarn has clearly formed by mass transfer of Si, Al, Fe, Mg, and Ti from the diorite and Ca in the reverse direction from the marble. The genesis of the skarn is currently being investigated, with particular emphasis placed on such aspects as the thermal history, fluid compositions, and mass transfer processes (diffusion versus infiltration metasomatism), using mineral chemistry data, stable isotopes and fluid inclusion methods. The exoskarns appear the most useful because of the abrupt changes from the inner melilite-dominated through the wollastonite-dominated to the massive tilleyite in contact with marble. In this respect the tilleyite skarn is particularly significant in that it represents the relatively simple system $CaO-SiO_2-CO_2$, with temperature/X_{CO_2} limits of tilleyite tightly constrained relative to wollastonite-calcite and spurrite or rankinite assemblages (Zharikov and Shmulovich, 1969; Treiman and Essene, 1983). However, in a mass transfer situation, published experiment data for specific reactions involving such minerals can be misleading. For example, for fig. 4 it would appear that massive tilleyite would form at a higher relative temperature than a melilite or wollastonite-dominated skarn. But the relative position of the massive tilleyite in contact with marble at the extremity of the Redcap skarn (and similarly at the Akagene Mine) suggests it formed at temperatures lower than the other exoskarns. Tilleyite can theoretically exist at temperatures as low as 320 °C at 1 bar (Treiman and Essene, 1983) and has been synthesized at 450°, 1 kbar by Henmi and Henmi (1978). However, given the mass transfer processes involved in skarn genesis, a more realistic approach is to view skarn sequences in terms of chemical potential and activity gradients (Korzhinskii, 1959, 1970; Thompson, 1959, 1970). For example, from figs. 1 and 5 of Pertsev (1974), the observed sequence of exoskarns at Redcap Creek can be

TABLE II. *Cell parameters and standard errors of natural tilleyites*

a	*b*	*c*	*β*	Location
15.111(5) Å	10.242(2) Å	7.577(2) Å	105.15(2)°	Barnavave, Carlingford, Ireland. (Louisnathan and Smith, 1970)
15.108(3)	10.241(1)	7.579(1)	105.17(1)°	Crestmore, California, USA. (Louisnathan and Smith, 1970)
15.110(3)	10.241(2)	7.578(1)	105.15(1)°	Redcap Creek, Queensland, Australia

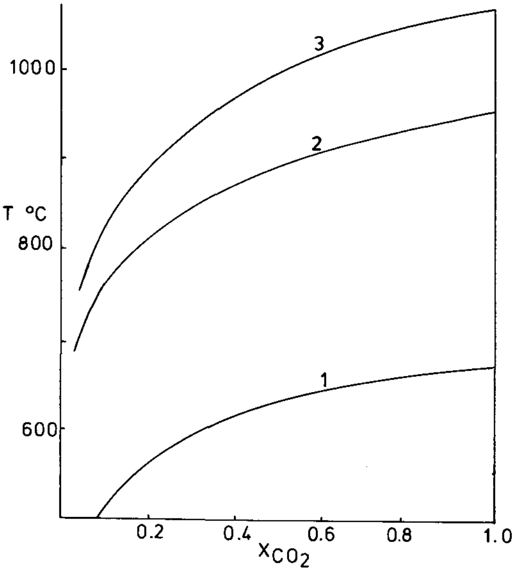

FIG. 4. T/X_{CO_2} plot at 1 kbar for selected reactions. 1. Calcite + quartz = wollastonite + CO_2 (Harker and Tuttle, 1956). 2. Diopside + calcite = akermonite + CO_2 (Walter, 1963). 3. Wollastonite + calcite = tilleyite + CO_2 (Treiman and Essene, 1983).

explained in terms of a gradient in a_{SiO_2} at low X_{CO_2} and fairly low $a_{Al_2O_3}$, at temperatures around 800 °C or higher for the tilleyite skarn.

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