Chapter 6

Volcanic influences on the formation of iron oxide±silica units in a VHMS terrain
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6.1 Introduction

Iron oxide±silica rocks form the ore equivalent horizon, or favourable stratigraphic position, within the host succession to many volcanic-hosted massive sulfide (VHMS) deposits and have long been considered a potential marker horizon in mineral exploration (e.g. Large, 1992). Such rocks are associated with many Australian VHMS deposits, including Highway-Reward (Fig. 6.1), Mount Morgan (Taube, 1986; Taube and Messenger, 1994, Messenger and Taube, 1994), Thalanga (Duhig et al., 1992a,b), Mount Chalmers (Large and Both, 1980; Hunns, 1994; Hunns et al., 1994), Scuddles and Gossan Hill (Ashley et al., 1988; Barley, 1992) and Captains Flat (Davis, 1975). The iron oxide±silica rocks may form the ore equivalent volcano-sedimentary units (e.g. Mt Morgan), occur as veins and massive replacements of volcanic host rocks (e.g. Highway-Reward), or occur within a 10 to 50 m thick interval which includes the ore horizon (e.g. Thalanga, Large, 1992). The iron oxide±silica rocks are sometimes laterally separated from mineralisation by a few tens to hundreds of metres (e.g. Duhig et al., 1992a,b) and not all iron oxide±silica units are associated with mineralisation. Similar iron oxide±silica rocks mark the ore equivalent horizon of some Canadian VHMS deposits (e.g. Ridler, 1971), and Japanese Kuroko deposits (Kalogeropoulos and Scott, 1983; Fig. 6.1F).

Recent observations of the seafloor confirm the presence of a variety of Fe-Si enriched hydrothermal precipitates. They may occur as chimneys, thin sediment layers/beds, irregularly shaped mounds, or fill fractures within lavas (Hekinian et al., 1993). Such units are forming around actively venting sulfide mounds at mid-ocean ridge spreading centres and have been mapped at the East Pacific Rise (Barrett et al., 1988; Juniper and Fouquet, 1988; Boyd et al., 1993; Hekinian and Fouquet, 1985; Hekinian et al., 1993; Alt et al., 1987; Janecky and Seyfried, 1984), the FAMOUS site on the Mid-Atlantic Ridge (Juniper and Fouquet, 1988), the Juan de Fuca Ridge (e.g. Normark et al., 1983; Tivey and Delaney, 1986; Hannington and Scott, 1988) and the Galapagos Spreading Centre (Herzig et al., 1988). Similar iron oxide±silica deposits have been recorded at the Valu Fa Ridge, Lau Basin (Fouquet et al., 1993), the Okinawa Trough (Juniper and Fouquet, 1988) and submarine volcanoes of the Society Islands, South Pacific (Boyd et al., 1993; Hekinian et al., 1993). Others are associated with silicic to intermediate submarine volcanic settings including the PACMANUS site, western Woodlark basin (Binns et al., 1993; Boyd et al., 1993).
There is clearly a spectrum of iron oxide-silica deposits/rocks in host successions to VHMS deposits. A detailed study of iron oxide-silica rocks and alteration in the Trooper Creek Formation between Coronation homestead and Trooper Creek prospect, has led to a better understanding of the relationships of the iron oxide-silica rocks to mineralisation and the volcanic host successions. This research builds on earlier work by Duhig et al. (1992a,b) and demonstrates that many of the iron oxide-silica rocks are sub-seafloor replacements of rhyolite and dacite, peperite, stromatolitic and oncolitic units and pumiceous units (Fig. 6.1G-I). In this chapter, terminology is reviewed, the involvement of iron oxide secreting micro-organisms in iron oxide-silica deposition is assessed, and the role of volcanic facies and volcanism on iron oxide-silica precipitation discussed.

Figure 6.1 (A-E) Cartoon showing the distribution of ironstone lenses associated with several VHMS deposits. Data from Horikoshi (1969), Taube (1986), Large and Both (1980), Duhig et al. (1992b), Sainty (1992), Large (1992) and the present study. (F-H) Schematic representation of the lithofacies associations hosting iron oxide-silica units in the study area.
6.2 Terminology and the description of iron oxide±silica rocks/deposits

Iron oxide±silica rocks and alteration in volcanic successions have been variably termed exhalite, ironstone, jasper, jaspilite, chemical sediment, ochre, umber and ferruginous chert. The term "tuffaceous exhalite" has been used for iron oxide±silica rock which overlies some of the Noranda deposits in Canada (e.g. Kalogeropoulos and Scott, 1983) and "tetsusekiei" (literally "iron quartz") which overlies some Kuroko deposits (e.g. Kalogeropoulos and Scott, 1989), in recognition of the volcanioclastic components in these deposits. Exhalite (Ridler, 1971) is a genetic interpretive term and is not suitable for description of iron oxide±silica rocks for which an exhalative origin cannot be clearly demonstrated. In sedimentary classifications, an ironstone is a rock containing > 15 wt% Fe (James, 1954). In the current study, the term ironstone has been used to refer to massive or laminated iron oxide±silica-rich rock with or without a sedimentary or volcanic component. The term tuffaceous ironstone is adopted for ironstone which contains a recognisable volcanioclastic component (e.g. shards, pumice, scoria, crystals) or alteration products of a former volcanioclastic component.

Intense pervasive hematite alteration occurs at the margins of the Highway-Reward massive sulfide deposit, as stratiform zones beneath some ironstones, as discontinuous pods in andesitic scoria breccia and at the margins of lava domes and cryptodomes. The term iron oxide±silica alteration/rock is adopted here as a non-genetic general descriptive term that can be applied to hematite-altered volcanic rock, ironstone and tuffaceous ironstone.

6.3 Stratigraphic distribution of ironstones in the Seventy Mile Range Group

Small (1-60 m) discontinuous lenses and pods of ironstone are common in the Seventy Mile Range Group (Duhig et al., 1992b; Berry et al., 1992). In the area west of Thalanga mine, ironstones occur in three stratigraphic positions (Duhig et al., 1992b): at the contact between the Puddler Creek Formation and rhyolites of the Mount Windsor Formation; within the Thalanga ore horizon at the contact between the Mount Windsor Formation and the overlying Trooper Creek Formation; and within the Trooper Creek Formation, 80-100 m above the Thalanga ore position.

Elsewhere in the Seventy Mile Range Group, ironstones are largely restricted to the Trooper Creek Formation or occur at the contact between the Trooper Creek Formation and the overlying Rollston Range Formation (Fig. 1.1; Duhig et al., 1992b; Berry et al., 1992; Doyle, 1996). In the study area, ironstones are restricted to the middle and upper
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Trooper Creek Formation, cropping out at Trooper Creek prospect and along strike 1.6 km to the west, north of Trooper Creek prospect, and at Highway East and Handcuff (Map 1). At Highway-Reward, iron oxide±silica alteration/rock occurs in drill core and at the base of the Highway pit.

6.4 Occurrence and volcanic facies

In the study area, iron oxide±silica alteration/rock is associated with different volcanic facies (Fig. 6.1). Four principal facies associations are important. (1) The stratified andesitic breccia and sandstone facies association comprises graded andesitic scoria breccia, cross-stratified andesitic breccia and sandstone, and globular clast-rich andesitic breccia. These units deposited from subaqueous mass flows and by fallout from strombolian eruptions (Chapter 4). (2) The second facies association was sourced from explosive rhyolitic to dacitic eruptions and comprises planar laminated dacitic pumice breccia (water-settled fallout) and graded lithic-crystal-pumice breccia and sandstone (sediment gravity flow deposits; Chapters 4 & 5). (3) Associations of rhyolitic to dacitic coherent facies, peperite and autoelastic breccia which form lavas, domes and cryptodomes. (4) Massive and laminated siltstone units.

Table 6.1 summarises the character and lithofacies associations of iron oxide±silica alteration/rock in the study area. Only the best exposed localities are described in the subsequent sections. The ironstone units are more often hosted by volcaniclastic and sedimentary facies rather than coherent facies, but do not appear to be preferentially associated with one lithofacies type. However, the thickest and longest ironstone lenses are hosted by rhyolitic to dacitic pumice breccia and sandstone units.

6.4.1 Ironstone lenses in rhyolitic to dacitic pumice breccia and sandstone

At Trooper Creek prospect, ironstone occurs at the contact between stratified andesitic breccia facies association and overlying planar laminated dacitic pumice breccia units, forming a discontinuous conformable horizon (horizon 1) approximately 500 m in length (Figs. 6.2–6.3). There is evidence for palaeotopography on the contact between the andesitic breccia and overlying dacitic pumice breccia (Chapter 4). The ironstone lenses occur on both the palaeotopographic highs and palaeotopographic lows. The lenses range in thickness from 1 cm to 10 m and although mostly 10 to 20 m in exposed (actual?) length, one lens has a strike length of approximately 116 m. Detailed mapping of the best exposed sections of horizon 1 ironstone (Figs. 6.3–6.5A) suggests that the lenses occur at
Table 6.1: Significant iron oxide/silica occurrences in the Trooper Creek Formation between Coronation homestead and Trooper Creek prospect.

<table>
<thead>
<tr>
<th>Prospect</th>
<th>Locality</th>
<th>AMG reference</th>
<th>Occurrence</th>
<th>Character</th>
<th>Samples</th>
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<td>7741900 mN,</td>
<td>dacitic pumice</td>
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<td>95-206, 95-207, 95-208, 95-210, 95-213, 95-273, 95-276</td>
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<td></td>
<td>Trooper Ck</td>
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<tr>
<td></td>
<td>cattle yard</td>
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<td>above stratified andesitic</td>
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<td>breccia</td>
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<td>breccia</td>
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<td>coherent &amp;</td>
<td>veinlets</td>
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<tr>
<td></td>
<td>DDH HDD</td>
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<td>massive with</td>
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Figure 6.2 Simplified geological map showing the distribution of ironstone lenses and volcano-sedimentary units in the southern part of Trooper Creek prospect.
Figure 6.3 Detailed outcrop map showing the distribution of the principal lithofacies and iron oxide-silica horizons at Trooper Creek prospect (around 7741900 mN, 426800 mE). Locations of sections A-C are shown in Figure 6.2.
Figure 6.4 Measured sections presented as graphic logs for major lithologies in the Trooper Creek Formation in the area of the Trooper Creek Prospect. Locations of sections A-E are given in figures 6.2 and 6.3.
Figure 6.5 Outcrop maps showing the distribution of ironstone lenses and their relationships to the enclosing volcanic facies. (A) Horizon 1 ironstone in the western part of the Trooper Creek prospect ("western lenses"). Locality shown in figure 6.2. (B) Ironstone lenses at "cattle yard" (around 7743700 mN, 424600 mE).
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the base, top or are enclosed by the planar laminated dacitic pumice breccia facies. The pumice breccia is non-welded, diffusely laminated and comprises pumice clasts, shards, crystals and crystal fragments (plagioclase) (Chapter 4). The crystal composition suggests a dacitic composition. Top contacts of the ironstone lenses are sharp and sometimes overlain by hematite-altered siltstone. However, bottom contacts vary from sharp to gradational with massive ironstone (Fig. 6.6A) passing through tuffaceous ironstone (Fig. 6.6B) into sericite-hematite-altered, dacitic pumice breccia or stratified andesitic breccia (Fig. 6.6C). Laminae within the altered pumice breccia can be traced into tuffaceous ironstone. Within a 45 cm wide zone beneath the ironstone lens, the pumice breccia contains abundant hematite nodules, 1-5 mm in diameter.

Tuffaceous ironstone comprises non-volcanic quartz and hematite and relic pumice fragments, shards and crystals. Quartz-hematite-rich patches and bands alternate with quartz-dominant pyroclast-rich patches and bands, accentuating the primary laminated fabric (Fig. 6.6B). One segment of horizon 1 ironstone contains microbialites (stromatolites and oncolites; Figs. 6.3 & 6.4). The stromatolites occur as domed biostromes (1-3 cm thick) that contain oncolites as well as pyroclastic components (Chapter 4). Microbialites in the ironstone are now quartz-hematite, whereas pumice clasts and shards are pervasively silica-sericite-altered and outlined by fine-grained hematite (Fig. 6.6D).

A poorly exposed, 28.7 m thick sequence of planar laminated siltstone and polymictic lithic-pumice breccia (Chapter 4) separates horizon 1 ironstone from a second thin (10-30 cm), stromatolitic and oncolitic ironstone horizon (horizon 2, Fig. 6.3). The polymictic lithic-pumice breccia is poorly sorted, matrix-supported and weakly graded. The breccia contains clasts of dacite, laminated siltstone and ironstone. Strong hematite alteration of the pumiceous matrix obscures textures in the upper part of the unit. The internal organisation is consistent with deposition as a sediment gravity flow. Ironstone clasts in the breccia were incorporated at source or collected from the substrate during transport (Chapter 4).

Horizon 2 ironstone is very poorly exposed and comprises in situ stromatolites which are built on silicified sandstone and pebble conglomerate units containing oncolites, stromatolite clasts (0.3-12 cm) and pyroclastic components (Fig. 6.4 – section B). The in situ stromatolites occur as domed bioherms, 6-7 cm high and up to 8 cm in diameter (Chapter 4). The intercolumn matrix is a mixture of unaltered feldspar crystal fragments, lithic grains and pumice fragments. The bioherms are overlain by pervasively hematite-altered siltstone. Stratified dacitic pumice breccia and sandstone beds occurs above the
Figure 6.8

Photomicrographs of ironstone units from the Trooper Creek Formation.

(A) Coalescing type 1 spherules surrounding a cuspate hematite patch. Fans of fibres (arrow) project out from the margin of spherules into the hematite patch suggesting that both the bundles of fibres and the hematite are space filling. Plane polarised light. 95-210; Trooper Creek prospect; 7741900 mN, 426800 mE.

(B) Botryoidal texture in tuffaceous ironstone. Alternating concentric quartz- and hematite-rich laminae nucleate around a hematite core. The remainder of the photomicrograph comprises hematite patches separated by finely crystalline quartz. Plane polarised light. 95-275; Trooper Creek prospect; 7741900 mN, 426800 mE.

(C) In this sample of massive ironstone, patches of spherules (s) and hematite are separated by an apparent matrix of fine-grained recrystallised quartz (r). Occasional relic domains of spherules are identifiable in some parts of the apparent matrix (arrow) and are separated by small cuspate hematite patches. Plane polarised light. 95-210; Trooper Creek prospect; 7741900 mN, 426800 mE.

(D) Occasional pumice clasts and shards are preserved in this sample of massive ironstone. The pumice fragments (p) are now quartz and are outlined by hematite. Hematite has completely replaced pumice fragments in some parts of the sample. Plane polarised light. 95-273; Trooper Creek prospect; 7741900 mN, 426800 mE.

(E) Pumice fragments and shards in this sample are now fine-grained quartz and are delineated by hematite. The pyroclasts have compacted and deformed around a large quartz nodule (n) which grew within the pumice breccia during replacement by quartz and hematite. Plane polarised light. 95-212; Trooper Creek prospect; 774200 mN, 426100 mE.

(F) Photomicrograph of hematite-sericite-altered pumice breccia. The pumice clasts and ovoid vesicles (arrow) within them are outlined by hematite. The vesicles and formerly glassy walls are now sericite. The breccia also contains hematite patches. Plane polarised light. 95-204; Trooper Creek prospect; 7741900 mN, 426800 mE.

(G) This sample comes from an ironstone pod in rhyolite. Relic coalescing spherules are separated by cuspate hematite patches. Many spherules have recrystallised to fine-grained quartz. Plane polarised light. 95-150, north of Trooper Creek prospect; 7743500 mN, 428160 mE.

(H) Photomicrograph of filaments (arrow) in a quartz-hematite vein cutting coherent dacite. 94-61; Handcuff; 7749500 mN, 418950 mE.
siltstone. Intense pervasive hematite-alteration of the lower 2 m of the pumice breccia has destroyed most primary textures in this part of the unit (horizon 3).

Horizon 4 ironstone is exposed 216 m to the west of horizons 1-3 (Fig. 6.4 - section E), and overlies stratified andesitic breccia containing bomb fragments (globular clast-rich andesitic breccia facies; Chapter 4). The ironstone has a granular sandy texture, with dark maroon hematite-rich patches (1 to 5 mm long) separated by a quartz-rich apparent matrix. Thin-sections reveal rare relict shards. Scoria breccia beneath the ironstone lens is intensely quartz-hematite-altered within a metre of the contact, and variably sericite-hematite-altered to 130 m below the contact. Hematite alteration is most intense within 26 m of the ironstone, obscuring clast margins and generating an apparent fine-grained sandstone.

6.4.2 Iron oxide±silica alteration/rock and stratified andesitic breccia

In a 1 m wide zone beneath horizon 4 ironstone, stratified andesitic breccia contains a network of quartz-hematite domains which replace the matrix of the breccia (Fig. 6.6E). The pod encloses (Fig. 6.6E). At Highway East prospect (around 7747350 mN, 420000 mE), stratified andesitic breccia includes zones of intense pervasive hematite alteration. Although ironstone is not exposed, the intensity of hematite alteration is similar to that associated with ironstone lenses at Trooper Creek prospect, and the alteration may be a lateral or vertical equivalent of an unexposed or poorly developed ironstone.

6.4.3 Ironstone associated with lavas, domes and cryptodomes

Northwest of Trooper Creek prospect (around 7743700 mN, 424600 mE), pods of ironstone (1-3 m) are enclosed in massive coherent rhyolite. The ironstone pods have sharp margins and an apparent clast-in-matrix texture in which equant, irregular and ovoid hematite-rich “grains” are enclosed in a hematite-poor, quartz-rich, apparent matrix (Fig. 6.6F). Parts of the ironstone (2 to 10 cm across) are devoid of the apparent clastic texture and comprise a mosaic of quartz and hematite. Rhyolite surrounding the ironstones is purple in colour due to pervasive hematite alteration, but away from the pods is sericite-chlorite-altered. Quartz-hematite veins cut the rhyolite along contacts with the ironstone. The rhyolite is quartz- and feldspar-phyric and consists almost entirely of coalescing spherical spherulites (60-200 μm). Partial recrystallisation to interlocking anhedral quartz and feldspar has destroyed some microstructures in many of the spherulites. Cuspate areas (10-250 μm) of hematite occur between some coalescing spherulites and along the
Margins of quartz and feldspar phenocrysts in the groundmass. The hematite patches are presumably altered glass.

Field relationships and drill hole sections in the Handcuff area (around 7748600 mN, 417850 mE) show that some ironstone lenses and rhyolite units are spatially, and possibly genetically, related. At one locality (around 7743700 mN, 424600 mE) the ironstone lenses occur within massive or laminated siltstone at the margin of a rhyolite syn-sedimentary intrusion. The ironstone is massive or comprises alternating hematite-rich and quartz-rich bands (laminae?). The rhyolite is mostly sericite-chlorite-quartz-altered, but along some contacts with the ironstone lenses both the rhyolite and siltstone are hematite-altered and contain disseminated pyrite (< 1 mm). In diamond drill hole HDD 012 (25-100 m), quartz-hematite veinlets cut across chlorite-sericite-quartz-altered rhyolite and peperite. Rhyolite along the margins of the veins is intensely silicified. In Handcuff diamond drill holes HDD 007 (372-410 m) and HDD 022 (262-275 m), quartz-hematite veins occur in massive coherent dacite and monomictic dacitic breccia. The breccia is non-stratified and comprises angular blocky fragments. Clasts have mostly altered to sericite and chlorite, whereas the matrix has altered to quartz-hematite. The textural characteristics and contact relationships are consistent with interpretation of the breccia as hyaloclastite at the margins of a lava (Chapter 5). At Handcuff (around 7747400 mN, 417250 mE), peperite along the top contact of a partly extrusive cryptodome provides evidence for mixing of dacite and hematite-rich siltstone and sandstone. Dacite clasts in the peperite are sericite-altered and separated by iron oxide-rich siltstone (Fig. 6.6G). Laminae in the siltstone/sandstone are absent in the peperite but are preserved 0.5-1 cm away from the contact. The laminae are purple and hematite-rich or are pale and sericite-altered. Hematite occurs only in the siltstone suggesting that it is not an alteration phase but deposited as the siltstone accumulated. The dacite mixed with the siltstone while it was still poorly consolidated (Chapter 5), destroying bedding in the siltstone at the contact.

In Highway diamond drill hole REW 803 (31.55-130 m), dacite includes irregular bifurcating seams of siltstone and jigsaw-fit aggregates of dacite clasts that are separated by siltstone. The breccia facies is gradational into massive coherent dacite. Siltstone in the peperite is locally quartz-hematite-rich and veins of quartz-hematite-carbonate dissect the core. A silicified halo up to 4 cm wide surrounds some of the veins, suggesting that they are replacements of the dacite and are not sediment which mixed with the dacite during fragmentation.
6.4.4 Ironstone lenses in siltstone

At Handcuff prospect (around 7748750 mN, 417750 mE), massive and finely laminated, silicified, siltstone contains minor thin (2-5 mm), dark red, hematite-rich laminae. North of Handcuff prospect (around 7749320 mN, 418100 mE), massive and weakly planar laminated silicified siltstone includes lenses of ironstone up to 30 m in length. The lenses form a bedding-parallel horizon in the hinge of a steeply SSW plunging syncline. The ironstones are massive or patchy, hematite-rich and contain cubic pits after pyrite. Ironstone lenses are separated by finely laminated siltstone containing small (5 to 20 cm) hematite-rich patches with diffuse margins, alternating light grey and green–grey silicified bands and discontinuous, bedding-parallel, hematite-rich bands. The hematite-rich bands consist of irregular, round or ellipsoidal hematite-rich patches which are separated by quartz-rich domains. Thin (2-3 mm) semi-continuous hematite-rich bands (? laminae; Fig. 6.6H) are locally present.

6.4.5 Indeterminate facies relationships

In some cases, contacts between ironstone lenses and volcanic facies are not exposed. To the west of Trooper Creek (around 7743700 mN, 414600 mE), a series of massive ironstone lenses are exposed discontinuously over a strike length of 175 m (Fig. 6.5B). At Highway East prospect (around 7746600 mN, 418250 mE), ironstone lenses occur near outcrops of rhyolite but contacts are not exposed.

6.5 Ironstone mineralogy and textures

The mineral assemblages associated with massive ironstone and tuffaceous ironstone are different. Petrography combined with X-ray diffraction (Appendix E1) show that quartz, hematite and locally fine-grained (5 μm) magnetite are the principal components of massive ironstone. In addition to quartz, hematite and magnetite, various assemblages of epidote, sericite, chlorite, albite, calcite, sanidine and plagioclase feldspar are present in tuffaceous ironstone and stromatolitic ironstone.

Ironstones have textures which can be subdivided into three main groups: (1) those reflecting a volcanic input or precursor; (2) textures recording biological activity in the depositional environment; (3) non-volcanic and non-biological textures, here defined as chemical textures. Many ironstones are characterised by textures from more than one group, and by different textures from the same group. Textures in ironstones associated
with each of the principal volcanic facies can be similar, but others are unique to a given facies association or ironstone outcrop. During metamorphism and tectonic deformation, earlier mineral assemblages were recrystallised or replaced by coarse metamorphic minerals, thus destroying or modifying primary (volcanic, biological, chemical) textures (cf. Duhig et al., 1992b).

6.5.1 Volcanic textures and their altered equivalents

*Pumice and shards:* Tube pumice in the ironstones is blocky with ragged ends and smooth planar margins. Most of the glass shards have cuspatc and microvesicular pumice shapes, but a few platy shards occur. In areas of strong sericite-chlorite alteration, the pumice fragments and former vesicles within them are delineated by fine hematite. Quartz-hematite has replaced former glassy vesicle walls and vesicles are filled with quartz, hematite, sericite, or zones of hematite-quartz-sericite (e.g. 95-203). Some pumice clasts have been partially replaced by hematite and have apparent blocky shapes. In these clasts, vesicle textures have been destroyed but the clast margins are preserved (e.g. 95-203). Many phyllosilicate-altered pumice clasts are compacted and deformed around quartz-hematite-altered pumice clasts and feldspar crystals. The compacted pumice clasts define bedding-parallel compaction foliation.

*Crystals and crystal fragments:* In ironstone, feldspar (sanidine and plagioclase) crystals and crystal fragments are largely unaltered, or only weakly altered. Sericite has partially replaced feldspar in a few samples and rarely (e.g. 95-200) polycrystalline quartz has replaced a tabular mineral, which may have been feldspar. Epidote has replaced fragments of an unidentifiable ferromagnesian mineral.

6.5.2 Biological textures

*Microbialites:* At Trooper Creek prospect, microbialites in ironstone comprise stromatolites and oncolites (Chapter 4). The oncolites are elliptical to spherical and vary from 0.5 to 1.5 cm across. The component laminae are arranged around a central nucleus which is often a pyroclast or lithic fragment. Stromatolites are characterised by fine (8-20 μm), relatively flat internal laminae. Non-columnar varieties have flat-laminated, undulatory, pseudo-columnar, cumulate or columnar layered forms (Chapter 4). Branching and non-branching columnar stromatolites are also present. The laminae comprising stromatolites and oncolites are typically very thin (8-20 μm) and quartz-rich or hematite-rich.
Filamentous structures: Branching networks of filaments are preserved in a few ironstone samples and in quartz-hematite veins in dacite (Chapter 4). The filaments are randomly oriented, 10 to 200 µm long, with cylindrical cross-sections, 5-8 µm in diameter. Filament walls are delineated by hematite granules, and quartz (5-500 µm) fills the interstitial space. The filaments are similar to those described and interpreted by Dahig et al. (1992a,b) as iron oxide-secreting bacteria and/or fungi.

Other biological structures: Fragments of trilobites are preserved in one sample of stromatolitic and oncolitic breccia (Chapter 4). Other microfossils include possible sponge spicules, a single gastropod and a possible brachiopod (95-200; Chapter 4). The fossils are now cryptocrystalline quartz±hematite and delineated by hematite.

6.5.3 Chemical textures

Spherules: Spherules (50-200 µm diameter) in ironstone have been classified on the basis of the relative proportions and distribution of quartz to hematite, as well as on internal structure. Eight principal morphologies are recognised and their characteristics are summarised in Table 6.2 and Figure 6.7. Type 1A and 1B (Figs. 6.7A, 6.8A) spherules are composed only of quartz or albite, whereas the other spherule types are fine intergrowths of quartz and hematite. Type 2 and 3 spherules are characterised by a radial fibrous texture which is defined by variations in the abundance of radial hematite flecks. Similar radial fibrous textures characterise the core (type 4 spherules) or rim (types 5 and 6) of spherules which are concentrically zoned. Cores are opaque and hematite-rich, whereas rims are quartz-rich with hematite present as single granules and flecks, or else arranged in trails. Neither the hematite core nor the thin quartz rim of type 7 spherules are radially fibrous. In type 8 spherules, the cores comprise concentric quartz- and hematite-rich bands and rims are radially fibrous (Fig. 6.7A).

Isolated spherules are commonly spherical. Adjacent spherules may impinge on each other, producing elongate single or branching trains and coalescing patches. Domains (20 µm to 2 mm) of hematite occur between coalescing spherules and have cuspatate shapes (Fig. 6.7B-C). Fan- to sheaf-shaped bundles of radial quartz and hematite fibres occur around the outer margin of some domains of coalescing spherules and project into large hematite patches (Figs. 6.7D & 6.8A). In some samples, similar bundles of fibres radiate out from a line, forming axiolite-like structures (e.g. 95-179).

Metamorphism has destroyed or obscured the primary textures in many spherules. Initially, the centres of spherules recrystallise to interlocking anhedral quartz and in some
Table 6.2 Distinguishing characteristics of the eight spherule types identified in ironstone.

<table>
<thead>
<tr>
<th>Spherule</th>
<th>Size (µm)</th>
<th>Core</th>
<th>Rim</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1A</td>
<td>50-200</td>
<td>Core &amp; rim absent. Radially fibrous quartz or albite crystals nucleate out from centre.</td>
<td></td>
</tr>
<tr>
<td>Type 1B</td>
<td>50-60</td>
<td>Core &amp; rim absent. Finely crystalline quartz spherules.</td>
<td></td>
</tr>
<tr>
<td>Type 2</td>
<td>70-80</td>
<td>Absent. Sometimes centre is quartz dominant.</td>
<td>Increasing density of radially distributed hematite flecks &amp; granules towards hematite-poor margin.</td>
</tr>
<tr>
<td>Type 3</td>
<td>50</td>
<td>Granules of hematite form a ring in from margin.</td>
<td>Trails of hematite extend in from jagged spherule margin.</td>
</tr>
<tr>
<td>Type 4</td>
<td>100</td>
<td>Radially fibrous hematite flecks &amp; granules. Core and rim have similar width.</td>
<td>Quartz rim with minor hematite granules.</td>
</tr>
<tr>
<td>Type 5A</td>
<td>50-60</td>
<td>Hematite nucleus thinner than rim.</td>
<td>Radial quartz and hematite flecks and granules.</td>
</tr>
<tr>
<td>Type 5B</td>
<td>50-60</td>
<td>Opaque hematite nucleus. Core wider than rim.</td>
<td>Radial hematite flecks and granules between hematite nucleus and thin quartz rim.</td>
</tr>
<tr>
<td>Type 6</td>
<td>50-100</td>
<td>Hematite nucleus wider than rim.</td>
<td>Radial extinction of component anhedral quartz.</td>
</tr>
<tr>
<td>Type 7</td>
<td>100-250</td>
<td>Spherical, ellipsoidal to cuspat. Granular hematite ± minor quartz. Wider than rim (to 200 µm).</td>
<td>Quartz with disseminated hematite.</td>
</tr>
<tr>
<td>Type 8</td>
<td>50-100</td>
<td>Concentrally arranged hematite-poor bands and radially fibrous hematite-rich bands. Core narrower than rim.</td>
<td>Quartz with minor radial hematite flecks and granules.</td>
</tr>
</tbody>
</table>

Figure 6.7 (A) Cartoon of the principal spherule types (1-8) identified in ironstone. Not to scale. (B-D) Important textures in ironstone. (B) Coalescing, variably recrystallised type 1 spherules separated by cusptate patches of hematite. (C) Coalescing type 7 spherules. (D) Fans of quartz-hematite fibres projecting out from the margins of type 1 spherules into a patch of hematite.
cases, radial segments of the spherules become coarser grained. Further recrystallisation produces a mosaic of interlocking coarse-grained, anhedral quartz without fibrous textures. The round margins of recrystallised spherules are preserved along contacts with cuspatte hematite patches.

*Botryoidal texture:* Botryoidal texture comprises alternating concentric dark hematite-rich bands and light, hematite-poor, quartz-rich bands (Fig. 6.8B). Bands (<10 μm wide) are semi-continuous or discontinuous. In some samples, bands nucleate around single tube pumice clasts (e.g. 95-204), feldspar crystal fragments (e.g. 95-203) or hematite patches. The hematite patches are whole or form jigsaw-fit aggregates which are separated by cryptocrystalline quartz. Bands comprising botryoidal structures are smooth or have bulbous colloform-like shapes.

*Hematite patches and granules:* Hematite is mostly present as equant blocky to irregular patches surrounded by quartz (Fig. 6.8C). Wedge-shaped quartz-filled fractures extend in from the margins of the patches and are similar to cracks described in chert and attributed to the dewatering of silica gels (e.g. Schübel and Simonson, 1990). The hematite patches form jigsaw-fit aggregates or have elongate ragged shapes and are connected along mutual boundaries by thin stems. In some samples, the hematite patches contain small (5 μm), acicular, magnetite crystals. A few hematite patches are replacements of single pumice clasts. However, most iron oxide patches are not replacements of single pyroclasts and controls on their distribution are not obvious. Cuspatte hematite patches between spherules appear to be filling pore space or replacing a precursor space-filling mineral.

Chlorite patches within the ironstone lenses contain small (5 μm) round hematite “globules” (e.g. 95-273). In detail, the globules comprise smaller aggregates of very fine-grained “granular” hematite. Granular hematite is also present as fine disseminations in many quartz and hematite patches and in hematite-rich bands of botryoidal structures. Hematite delineating the margins and vesicles of pyroclasts is also granular.

*Quartz textures:* Quartz is the principal component of the ironstones and is texturally diverse (Duhig et al., 1992b). The following quartz polymorphs are adopted from Duhig et al. (1992b). Megaquartz is clear, equant to tabular, and greater than 200 μm across. Chalcedony is optically fibrous quartz which forms radial fibres, mostly around 100 μm long, in spherules or fan- to sheaf-shaped bundles. Microcrystalline quartz is equant, 1 to 100 μm across, and displays undulatory extinction and pinpoint birefringence. Cryptocrystalline quartz appears isotropic under cross polars and is less than 1 μm in grain size. Microcrystalline quartz and cryptocrystalline quartz are often yellow-brown to pink in colour, possibly due to a very fine dusting of hematite.
6.6 Ironstone textures and volcano-sedimentary facies

6.6.1 Ironstone associated with dacitic pumice breccia

Cross-sections through ironstone associated with dacite pumice breccia show that ironstone textures vary passing from massive ironstone, through pyroclast-rich ironstone, down into hematite-altered pumice breccia. Massive ironstone is dominated by domains of coalescing spherules (type 1B, 2, 5B, 6, 7 and/or 8) and cuspatate hematite patches (e.g. 95-179, 95-180). Recrystallisation of the spherules to interlocking medium grained (25 μm) or coarse-grained (400 μm) quartz has destroyed microstructures in many spherules and generates patches with only rare spherules (Fig. 6.8C). In a few samples (e.g. 95-179), quartz and hematite fibres are arranged in axiolite-like structures, separated by finely crystalline (5 μm) quartz (95-179).

In massive ironstone with relic volcanic particles (e.g. 95-273), pyroclasts are now composed of microcrystalline quartz, small type 1A spherules (e.g. 95-316) and/or delineated by hematite (Fig. 6.8D). In some samples, spherules cut across the margins of pumice clasts, shards and the vesicles within them. Microcrystalline quartz and megaquartz separate small irregular domains (200-700 μm) of coalescing spherules, hematite patches and rare botryoidal structures. The result in hand specimen is a fine granular texture. In one sample of horizon 1 ironstone (95-210), relic domains (500 μm) of calcite occur between patches of hematite and coalescing spherules. Light and dark bands (5-15 μm) in the calcite conform to contacts with the patches. Elemental maps from microprobe analysis show that zoning in the calcite is due to trains of very fine-grained (1-2 μm) anhedral quartz. Along the margins of the patches, recrystallisation to quartz-free calcite destroys original zoning in the calcite.

In tuffaceous ironstone, quartz-rich bands comprise coalescing type 2 spherules, fine (3-5 μm) quartz±hematite-altered pumice clasts, subordinate hematite patches and rare botryoidal structures. One sample (e.g. 95-214) contains branching networks of hematite filaments up to 200 μm long. The filaments project out from the margins of hematite patches and are enclosed by quartz. Single iron oxide globules at the ends of fibres may be cross-sections through filaments. Hematite-rich bands comprise single and interconnected hematite patches separated by finely crystalline (3-5 μm) quartz. Quartz nodules are also present (Fig 6.8E). The nodules have bulbous margins and comprise coarse quartz (25 μm), coalescing type 1 spherules and cuspatate hematite patches (25 μm across). Pumice fragments and shards are deformed around the nodules, suggesting that the nodules formed prior to compaction or else, grew within the pumice breccia and displaced the pyroclasts.
Figure 6.8

Photomicrographs of ironstone units from the Trooper Creek Formation.

(A) Coalescing type 1 spherules surrounding a cuspat e hematite patch. Fans of fibres (arrow) project out from the margin of spherules into the hematite patch suggesting that both the bundles of fibres and the hematite are space filling. Plane polarised light. 95-210; Trooper Creek prospect; 7741900 mN, 426800 mE.

(B) Botryoidal texture in tuffaceous ironstone. Alternating concentric quartz- and hematite-rich laminae nucleate around a hematite core. The remainder of the photomicrograph comprises hematite patches separated by finely crystalline quartz. Plane polarised light. 95-275; Trooper Creek prospect; 7741900 mN, 426800 mE.

(C) In this sample of massive ironstone, patches of spherules (s) and hematite are separated by an apparent matrix of fine-grained recrystallised quartz (r). Occasional relic domains of spherules are identifiable in some parts of the apparent matrix (arrow) and are separated by small cuspat e hematite patches. Plane polarised light. 95-210; Trooper Creek prospect; 7741900 mN, 426800 mE.

(D) Occasional pumice clasts and shards are preserved in this sample of massive ironstone. The pumice fragments (p) are now quartz and are outlined by hematite. Hematite has completely replaced pumice fragments in some parts of the sample. Plane polarised light. 95-273; Trooper Creek prospect; 7741900 mN, 426800 mE.

(E) Pumice fragments and shards in this sample are now fine-grained quartz and are delineated by hematite. The pyroclasts have compacted and deformed around a large quartz nodule (n) which grew within the pumice breccia during replacement by quartz and hematite. Plane polarised light. 95-212; Trooper Creek prospect; 774200 mN, 426100 mE.

(F) Photomicrograph of hematite-sericite-altered pumice breccia. The pumice clasts and ovoid vesicles (arrow) within them are outlined by hematite. The vesicles and formerly glassy walls are now sericite. The breccia also contains hematite patches. Plane polarised light. 95-204; Trooper Creek prospect; 7741900 mN, 426800 mE.

(G) This sample comes from an ironstone pod in rhyolite. Relic coalescing spherules are separated by cuspat e hematite patches. Many spherules have recrystallised to fine-grained quartz. Plane polarised light. 95-150, north of Trooper Creek prospect; 7743500 mN, 428160 mE.

(H) Photomicrograph of filaments (arrow) in a quartz-hematite vein cutting coherent dacite. 94-61; Handcuff; 7749500 mN, 418950 mE.
Ironstones

Ironstones 6.21

Pumice breccia beneath the ironstone lens is pervasively sericite-hematite-altered and contains hematite nodules, 2-5 mm across (Fig. 6.8F). Some nodules have bulbous margins and are massive with hematite-rich cores and thin (50-200 µm) quartz-rich margins. A few nucleate around weakly sericite-altered feldspar crystals or tube pumice fragments. The sericite-altered tube pumice fragments are deformed around the hematite nodules and define a bedding-parallel compaction foliation (S1).

6.6.2 Stromatolitic-oncolitic ironstone

Stromatolites and oncolites in ironstones are red in hand specimen due to replacement by hematite or alternating hematite-rich and quartz-rich laminae (Chapter 4). Finely crystalline quartz and subordinate disseminated granular hematite has replaced pumice fragments and shards trapped and bound within the microbialites. Pumice fragments are delineated by a hematite film or are entirely altered to hematite. Feldspar crystal fragments and epidote are also present. The remainder of the ironstone lenses consists of medium grained (20-50 µm) anhedral quartz. In one sample (95-218), polycrystalline quartz has replaced a lozenge-shaped crystal which may have been gypsum. Spherule textures are absent in stromatolitic ironstone.

6.6.3 Iron oxide-silica pods in stratified andesitic breccia

Horizon 4 ironstone at Trooper Creek is underlain by a small pod of hematite-rich, stratified andesitic breccia. Hematite occurs between the clasts and as small patches within the clasts. The margins of some clasts and the vesicles within them are delineated by a thin (2-5 µm) film of hematite. Spherules, botryoidal structures and filaments are absent.

6.6.4 Ironstone pods in rhyolite

Ironstone pods in rhyolite have a clast-in-matrix texture with hematite-rich "grains" separated by a quartz-rich apparent matrix. Most "grains" comprise coalescing spherules (types 2A, 6 or 8) and cuspat e patches of hematite (Fig. 6.8G). Other grains comprise an outer zone of coalescing round and fan- to sheaf-shaped spherules, and a hematite-rich core containing single spherules or branching trains of spherules. The remaining grains comprise equant jigsaw-fit aggregates of hematite patches separated by quartz or spongy mosaics of hematite and quartz. The apparent matrix between grains comprises fine-grained (25 µm) quartz which has locally recrystallised to coarse-grained (300 µm)
Ironstones. The apparent matrix locally contains relic spherules which are outlined by cuspatematches of hematite.

6.6.5 Quartz-hematite±carbonate veins in dacite

In carbonate-hematite-quartz veins (e.g. REW 803, 117.2 m), hematite occurs as thin (20 μm) rings around coarse-grained polycrystalline quartz patches (150-300 μm across). The quartz patches are separated by calcite. At the margins of the veins, sub-round hematite patches are intergrown with carbonate or quartz.

In quartz-hematite veins, hematite occurs as patches with bulbous margins or as fan- and sheaf-shaped bundles of fibres which are radially arranged around a hematite grain or patch. The hematite patches and fibres cut across boundaries between interlocking anhedral quartz crystals (20-200 μm across). The quartz is weakly peppered with granular hematite. Rare filamentous structures are preserved (Fig. 6.8H).

6.6.6 Ironstone in siltstone

Many ironstone lenses in silicified siltstone comprise hematite-rich patches (40-100 μm) separated by coarsely (100 μm) crystalline quartz (e.g. 94-401). Quartz occurs as interlocking crystals with 120° triple point junctions which suggest strong recrystallisation by metamorphism. Hematite-rich domains comprise euhedral fine-grained (5 μm) hematite and subordinate quartz.

6.7 Ironstone geochemistry

Detailed studies of the mineralogical and textural characteristics of the ironstone units provide a framework for geochemical studies using whole rock major, minor, trace and rare earth element (REE) analyses. The new data are presented in Appendix E2. Samples were first crushed in a jaw crusher and then powdered in a tungsten carbide disc mill. Major and trace element analyses were determined on a Philips automated XRF spectrometer at the University of Tasmania using standard fused disc and pressed pellets techniques (Norrish and Hatton, 1969; Norrish and Chappell, 1977). Ag and REE were determined by ICP-MS at ANALABS facilities in Perth. Samples (0.2 g) were digested in aqua regia/perchloric acid/hydrofluoric acid using ANALABS method 201. The major
Ironstone samples from the Trooper Creek Formation are principally composed of SiO₂ and Fe₂O₃ (Fig. 6.9A). All other oxides constitute less than 1 wt%, with the exception of Al₂O₃ which is high (4.6-8.7%) in some samples of massive, tuffaceous and stromatolitic ironstone. Single samples of tuffaceous ironstone from Trooper Creek prospect contain elevated K₂O (1.3%, 94-327) or MgO (2.3%, 95-275). Ratios of SiO₂/Fe₂O₃ are generally high (1.8-45) in massive ironstone, decrease (2.3-12) in tuffaceous and stromatolitic ironstone, and increase again in hematite-altered dacite pumice breccia (3.3) and a least altered equivalent (16.8; 95-308) (Appendix E2). Increasing concentrations of TiO₂, P₂O₅ and Al₂O₃ characterise the transition from massive ironstone to the least-altered equivalent (Fig. 6.9B-C). Ti/Zr ratios for the ironstone range between 16 and 40 but are mostly between 18 and 20, similar to the least-altered pumice breccia (95-308; Appendix E2). Variation in the ratios between samples may reflect initial compositional differences in the volcaniclastic precursor. Ironstone pods in rhyolite (95-150) have Ti/Zr ratios below detection limits and are significantly different to the rhyolite. This suggests that Ti and Zr have remained immobile and the ironstone pods contain little volcanic material.

Major element patterns for ironstone associated with pumice breccia, siltstone and rhyolite are generally similar (Fig. 6.10A). However, TiO₂ is low in ironstone associated with rhyolite, and ironstone lenses in pumice breccia contain elevated MgO. Trace element abundances vary between ironstone facies. Concentrations of Ba are higher in ironstone associated with siltstone (94-25, 94-401) than ironstone from other facies associations. Cu, Pb and Zn vary considerably between ironstone facies. One sample of ironstone associated with siltstone (94-401) contains anomalous Cu, Pb, Zn and Ag. Similar concentrations of Ba and Zn also occur in hematite-altered pumice breccia beneath horizon 1 ironstone (95-274) and in horizon 3 (94-334). V, Cr and Ni show a covariance with Fe (Fig. 6.11A-C). The highest values (V 1.3 wt%; Cr 26 ppm; Ni 18 ppm) occur in hematite-altered pumice breccia (94-334). Fe shows a negative correlation with Mn, and both Fe and Mn show a covariance with Ni (Fig. 6.11D). Sc, Sb, Bi and Ag are consistently low and mostly below detection limits (Appendix E2).

The composition of ironstone units from the study area is largely different from ironstone at Thalanga. Samples of ironstones associated with pumice breccia are enriched in MgO.
Ironstones

Figure 6.9 Major element plots for ironstone lenses in pumice breccia units at Trooper Creek prospect. Elemental concentrations vary systematically passing from hematite-altered pumice breccia, through tuffaceous ironstone, into massive ironstone. (A) Fe$_2$O$_3$ vs. SiO$_2$; (B) TiO$_2$ vs. Al$_2$O$_3$; (C) TiO$_2$ vs. P$_2$O$_5$. 
Figure 6.10 (A) Major element plot for ironstone associated with dacite pumice breccia at Trooper Creek Prospect, ironstone hosted by siltstone (Handcuff) and ironstone pods in a rhyolite lava (north of Trooper Creek prospect). (B) Major element patterns for the average composition of massive ironstone from Trooper Creek prospect and ironstone lenses at Thalanga. Data for Thalanga from Duhig et al. (1992b).
Figure 6.11 Selected trace element vs. major element plots for ironstones from the Trooper Creek Formation in the area between Coronation homestead and Trooper Creek prospect. (A) Fe₂O₃ vs. Ni; (B) Fe₂O₃ vs. V; (C) Fe₂O₃ vs. Cr; (D) Ni vs MnO.
Figure 6.12 Major element concentrations of ironstone associated with dacitic pumice breccia at Trooper Creek Prospect and (A) Noranda chemical and clastic layers; (B) Tetsukieki clastic and chemical layers; (C) modern seafloor deposits. Data from (1) Kalogeropoulos and Scott (1989); (2) Kalogeropoulos and Scott (1983); (3) Adachi et al. (1986); (4) Binn et al. (1993); (5) Barrett et al. (1988).
and K$_2$O and depleted in Na$_2$O, relative to ironstone from Thalanga (Fig. 6.10B). The low Na$_2$O content of ironstones associated with silstone distinguishes them from the ironstone lenses at Thalanga (Fig. 6.10A-B). Ironstone pods in rhyolite also have lower Na$_2$O values, in addition to higher CaO concentrations and lower K$_2$O abundances. Lithogeochemical studies of ironstone from the Kuroko and Noranda massive sulfide deposits were undertaken by Kalogeropoulos and Scott (1983, 1989). The major element patterns for ironstone from Trooper Creek prospect are similar to analyses from the "chemical layers" in ironstone from massive sulfide deposits in the Kuroko and Noranda districts (Fig. 6.12A-B). Variation in the concentration of MgO, CaO, Na$_2$O, K$_2$O and P$_2$O$_5$ in ironstone from the three districts, probably reflects differences in the composition of volcanic particles within the ironstone units. The major element patterns of ironstone from the Trooper Creek prospect and iron oxide-rich sediments from the modern seafloor are distinctly different (Fig. 6.12C). Adachi et al. (1986) demonstrated that hydrothermal Fe-Mn-Si units are readily distinguishable from non-hydrothermal precipitates by their low Al/ (Al+Fe+Mn) ratios. On a plot of Fe-Al-Mn, samples of ironstone from the Trooper Creek Formation plot within the hydrothermal field of Adachi et al. (1986) (Fig. 6.13).

![Figure 6.13 Al-Fe-Mn plot for ironstones from the Trooper Creek Formation in the study area. Samples (n=14) plot in the hydrothermal field for Fe-Mn-Si oxides defined by Adachi et al. (1986).](image-url)
6.7.2 Isocon analysis

Bulk chemical compositions of tuffaceous ironstone at Trooper Creek prospect cannot be equated with the composition of their precursor volcanioclastic units, because of major addition and/or depletion of Si, Fe and other elements. To determine the overall chemical changes with increasing alteration, a least-altered dacitic pumice breccia (95-308) from the stratigraphic section was compared with the average of each of its altered equivalents. The isocon method (Grant, 1986; Huston, 1988, 1993) provides a graphical method to determine compositional changes during alteration. In these calculations (Appendix E3), elements are ordered so that those usually considered immobile are evenly dispersed, and each element is assigned an integer (ni) in ascending order (e.g. SiO₂ = 1, Fe₂O₃ = 2). The scaled concentration of a particular element (C'i) can be calculated from:

\[
C'i = \frac{ni \times C'^i}{C'i}
\]  

(1)

where C'i is the concentration of an element in the altered rock for the corresponding integer value ni, and C'i = the concentration of an element in the unaltered equivalent for the corresponding integer value ni. The scaled values are plotted on the Y-axis against the corresponding integer which, for ease of interpretation, is replaced by the corresponding element symbol.

Once plotted the isocon can be determined by fitting a line through the immobile elements (Al, Ti, Zr, Nb and Y) and the isocon slope (m) calculated. The net mass change (M^A) relative to the least-altered equivalent can be calculated using:

\[
M^A (%) = 100 \left( \frac{1}{m} - 1 \right)
\]

(2)

Relative mass change for each element can be estimated from the isocon. Elements that gained mass through alteration plot above the isocon and those that lost mass plot below the isocon. The relative mass change for particular elements can be calculated by the relationship:

\[
C'^i (%) = 100 \left[ \frac{CAi}{(mCUi)} - 1 \right]
\]

(3)

where C'^i (%) is the relative mass change for the element corresponding to the integer ni.

The absolute mass change has not been calculated because the present density of the least-altered equivalent is different from that of the unaltered and uncompacted equivalent. The
interpretation of the isocon has several limitations (Huston, 1988, 1993): (1) the relative mass changes are calculated using a least-altered equivalent which was sourced from a different eruption than that hosting the ironstone, and so may be geochemically different; (2) the altered and unaltered lithofacies are resedimented volcaniclastic units and so probably have compositional variations unrelated to alteration; (3) the primary composition of the least-altered pumice breccia was probably modified during alteration and compaction. Samples of ironstone and the least-altered equivalent have similar Ti/Zr ratios, suggesting that they were originally geochemically similar. To minimise the effect of the second limiting factor, the average of multiple samples has been used in the calculations where possible (e.g. Huston, 1988, 1993).

The relative mass change of elements in massive ironstone (95-210, 95-276), tuffaceous ironstone (95-275) and hematite-altered pumice breccia (95-274) have been calculated for horizon 1 (Fig. 6.4 - section B). Massive ironstone is enriched in Si, Fe, Cr, Cu, Pb and Mn relative to the least-altered equivalent (Fig. 6.14A). Zn, Mg, Ca, P and Ba are also elevated. Sr, Rb, Na and K are depleted, while the high field strength elements reflect original magmatic concentrations. The tuffaceous ironstone sample has a similar geochemical pattern to massive ironstone. However, the relative gains in Si, Cr, Cu, Pb and Mn are less substantial (Fig. 6.14B). Tuffaceous ironstone is enriched in Mg compared to massive ironstone. The concentration of Sr, Rb, Ca and K are less than those in the least-altered equivalent and similar to samples of massive ironstone. Hematite-altered pumice breccia is enriched in Fe, Zn and Pb but much less so than overlying ironstone facies (Fig. 6.15A). Cu and Ba are also depleted relative to the least-altered equivalent. The net mass changes (M^A) relative to the least-altered equivalent is 1044.2 % for massive ironstone, 199 % for tuffaceous ironstone and -15 % for hematite-altered pumice breccia.

Samples of tuffaceous ironstone (horizon 1) from section B and localities further to the west (Fig. 6.5A) display similar relative mass changes. However, the western lenses are less enriched in Cu and Pb and depleted in Zn, Mn and Mg compared to samples from section B (Fig. 6.15B). Samples of stromatolitic ironstone display elemental patterns which are similar to massive and tuffaceous ironstone (Fig. 6.16A). However, stromatolitic ironstone is depleted in Zn and Mg. The concentrations of Rb, Na and K are low compared to the least-altered equivalent. The net mass change during alteration of stromatolitic ironstone is equal to a 270 % addition. Because the primary mineralogy of stromatolitic ironstone is different from the least-altered equivalent, direct comparison of analyses is not possible. Massive ironstone from horizon 4 is enriched in Mn and depleted in Nb and Zn, relative to both the least-altered equivalent (Fig. 6.16B) and massive ironstone from horizon 1. A net mass gain of 5570 % is indicated.
Figure 6.14 Isocon diagrams illustrating scaled concentrations of particular elements (1) and relative mass change for each element (2) in (A) massive ironstone and (B) tuffaceous ironstone from Trooper Creek prospect.
Figure 6.15 Isocon diagrams illustrating scaled concentrations of particular elements (1) and relative mass change for each element (2) in (A) hematite-altered pumice breccia and (B) massive ironstone from the western lenses at Trooper Creek prospect.
Figure 6.16 Isocon diagrams illustrating scaled concentrations of particular elements (1) and relative mass change for each element (2) in (A) stromatolitic ironstone from horizon 2 at Trooper Creek prospect and (B) massive ironstone from horizon 4.
Interpretation

The low concentration of elements other than SiO₂ and Fe₂O₃ reflects the dominance of quartz and hematite in the ironstone lenses. The decrease in the concentration of TiO₂, P₂O₅ and Al₂O₃ in the transition from massive ironstone, through tuffaceous ironstone, into hematite-altered pumice breccia, records the depletion of these elements during replacement/infiltration of the volcanic component by addition of quartz and hematite. The covariance between Fe and Ni, and Cr and V is tentatively interpreted to reflect adsorption by iron oxides. Ni abundances may indicate a seawater input by adsorption (Davidson et al., 1996). Isocon analysis identifies those elements which have been added by the hydrothermal fluid (and seawater) during alteration of the pumice breccia. These include Si, Fe, Cr, Cu, Zn, Pb, Mn, Mg and P. Cr may have been sourced from the underlying stratified andesitic breccia facies. Alteration of pyroclasts in the pumice breccia resulted in loss of Sr, Rb, Na and K.

6.7.3 Rare earth elements

Chondrite normalised (Boynton, 1984) rare earth element concentrations for ironstone samples from the study area are generally high (Figs. 6.17 and 6.18). Samples of ironstone with incomplete REE patterns have high LREE concentrations and HREE concentrations below detection limits (Fig. 6.18B-C). These include analyses of ironstone hosted by pumice breccia at Highway East prospect (94-246) and massive ironstone from east of Trooper Creek (95-130).

Samples of ironstone associated with pumice breccia are characterised by light rare earth element (LREE) enrichment and negative Eu anomalies (Fig. 6.17A). Single samples of massive ironstone (95-316), tuffaceous ironstone (95-212) and hematite-altered pumice breccia also display negative Ce anomalies (Fig. 6.17B-C). The transition from hematite-altered pumice breccia into massive ironstone is marked by a decrease in the concentration of both LREE and HREE. The different ironstone types generally have similar REE patterns and slopes (Fig. 6.17A). Massive ironstone with the smallest component of volcanic detritus (95-316) has the lowest concentration of REE, greatest negative Ce anomaly and Eu is below detection limit. Overall the REE patterns of the ironstones that are associated with pumice breccia are similar to rhyolitic and dacitic lavas and intrusions from the Trooper Creek Formation (Fig. 6.18A). The rhyolitic lavas have relatively flat to slightly LREE enriched patterns with shallower slopes than ironstone associated with pumice breccia.
Figure 6.17 Rare earth element plots of ironstone from Trooper Creek prospect normalized to the chondritic values of Boynton (1984). (A) Massive, tuffaceous and stromatolitic ironstone and hematite-altered pumice breccia from section B and horizon 4. (B) Massive ironstone from the section B (horizon 1) and horizon 4. (C) Tuffaceous ironstone from the section B (horizon 1) and the western lenses.
Figure 6.18 REE patterns normalized to chondritic values of Boynton (1984). (A) Comparison of ironstones from Trooper Creek prospect and Thalanga ore horizon (data from Duhig et al., 1992) with rhyolite and dacite from Highway-Reward (data from Stolz, 1991). (B) Ironstone associated with siltstone (Handcuff), forming pods in rhyolite and lenses in dacitic pumice breccia (Trooper Creek prospect). Ironstone from "cattleyard" is also plotted. (C) Ironstone associated with siltstone.
Ironstones

Ironstone from pods enclosed in rhyolite is enriched in LREE, depleted in HREE, and display negative Ce and Eu anomalies (Fig. 6.18B). The REE pattern of this sample (95-150) mirrors those of massive and tuffaceous ironstone. Massive ironstone associated with siltstone displays a variety of different patterns. Sample 94-25 shows slight LREE enrichment and a negative Ce anomaly. Two samples (94-18, 94-401) have positive Eu anomalies, similar to ironstone from Thalanga ore horizon and distinct from other ironstones in the study area. Sample 94-18 displays a U-shaped pattern with slight LREE and HREE enrichment and a weak positive Eu anomaly (Fig. 6.18C). Ironstone dominated by quartz (94-401) is characterised by a relatively flat LREE pattern, positive Eu anomaly and HREE depletion.

**Interpretation of rare earth elements**

Oxyhydroxide deposits with light REE enriched patterns and positive Eu anomalies are currently forming at hydrothermal vents on the modern seafloor (e.g. Michard et al., 1983; Michard and Albarède, 1986). The REE patterns of these deposits contrast with the surrounding sea water which is characterised by HREE enrichment, negative Ce anomalies, and much lower REE abundances (e.g. Alt, 1988). Some ancient equivalents (e.g. Duhig et al., 1992b) are also characterised by positive Eu anomalies and are interpreted as hydrothermal in origin. Other ironstone units display REE patterns which reflect input from both seawater (negative Ce anomalies) and hydrothermal fluids (positive Eu anomalies) (e.g. Graf, 1977; German et al., 1990; Barrett et al., 1990). Barrett et al. (1990) documented proximal to distal geochemical variations in hydrothermal precipitates on the Southern Explorer Ridge. They noted that iron oxyhydroxide deposits at the vent have hydrothermal signatures, whereas distal precipitates have seawater-modified Eu patterns. Hydrothermal particles scavenge REE from seawater as they are dispersed in the plume and following deposition (e.g. German et al., 1990; Olivarez and Owen, 1991). Post-depositional scavenging is limited by burial and so is less important if sedimentation rates are high (Olivarez and Owen, 1991).

Hydrothermal precipitates with positive Eu anomalies indicate that the hydrothermal fluids were enriched in divalent Eu and either, hotter than 250 °C, or reduced (Sverjensky, 1984; Lottermoser, 1989; Michard, 1989). Eu is sourced to the hydrothermal fluids during alteration of feldspar in the source rock. Hornblende, sphene, calcite and pyroxene are also sources of Eu (Rollinson, 1993; Barrett et al., 1990).

In the study area, samples of ironstone associated with pumice breccia typically have pronounced negative Eu anomalies. In tuffaceous ironstone, feldspar crystals are
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unaltered suggesting that the negative Eu anomalies are not related to the breakdown of feldspar. Feldspar crystals are rare in massive ironstone. However, samples of massive ironstone have weak negative Eu anomalies suggesting that Eu was relatively immobile (cf. McLennan and Taylor, 1979; Campbell et al., 1984; Schandl and Gorton, 1991). The negative Eu anomalies and hematite-rich composition of the ironstone lenses, suggest that the units deposited from oxidised and possibly low temperature (<100 °C) hydrothermal fluids in equilibrium with feldspar. Samples showing LREE enrichment and negative Eu and Ce anomalies reflect input from both the hydrothermal fluid and Cambrian seawater.

REE concentrations decrease passing from hematite-altered pumice breccia, through tuffaceous ironstone, into massive ironstone. However, the REE patterns for the different iron oxide±silica rocks are similar. The transition is interpreted to reflect the dilution of primary REE in a precursor pumice breccia by precipitation of quartz and other REE-poor minerals from the hydrothermal fluid. In hematite-altered pumice breccia, diagenetic compaction may have resulted in a relative increase in the concentration of REE relative to massive ironstone and tuffaceous ironstones, which altered early and remained uncompacted. Post-depositional scavenging of seawater-derived REE may have been important.

Ironstone associated with siltstone shows a range of REE patterns. Sample 94-25 displays slight LREE enrichment and a negative Ce and Eu anomaly, suggesting both seawater and hydrothermal REE sources. The remaining samples (94-18, 94-401) display positive Eu anomalies suggesting deposition from relatively hot (>250 °C) and/or reduced hydrothermal fluids. The weak enrichment in HREE in sample 94-18 may reflect a seawater input.

6.8 Discussion

6.8.1 Mechanisms and conditions of quartz-hematite deposition

In most ironstone units from the study area, textures (e.g. syneresis cracks and spherules; Fournier, 1985) and negative Eu anomalies, suggest precipitation of amorphous silica and hematite (or oxyhydroxide) from oxidised and low temperature solutions (<100°C; cf, Davidson et al., 1996). The exception is two samples (94-18, 94-401) which have positive Eu anomalies and sometimes contain pyrite and high Ba (94-401). These ironstone units deposited from relatively “hot” and/or reduced hydrothermal fluids. Along the mid-ocean spreading centres, amorphous silica is precipitated from seafloor hydrothermal fluids at low temperatures (15-100°C). The fluids evolve through mixing of
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relatively high temperature (175-350°C), silica-saturated hydrothermal fluids with cold seawater (Janecky and Seyfried, 1984; Tivey and Delaney, 1986; Alt et al., 1987; Hannington and Scott, 1988). At the Galapagos Rift (86°W), amorphous silica chimneys are forming at low temperatures (32-40°C), whereas amorphous silica intergrown with sulfides precipitates from fluids at 100°C (Herzig et al., 1988). Oxygen isotope studies suggest that tetsusekierie ores of Kuroko deposits also precipitated at less than 100°C (Tsutumi and Ohmoto, 1983). Most studies conclude that precipitation of amorphous silica proceeds by conductive cooling (e.g. Tivey and Delaney, 1986) or conductive cooling and mixing with seawater (e.g. Hannington and Scott, 1988; Herzig et al., 1988; Janecky and Seyfried, 1984). Hekinian and Fouquet (1985), examining massive sulfide fields on the East Pacific Rise near 13°N, suggested silica deposition during the waning stage of hydrothermal activity solely by mixing of low temperature (<100 °C), silica-rich solutions with seawater.

Silica solubility increases as solutions become more alkaline and in part, with increasing temperature and pressure (Williams and Crerar, 1985). In submarine environments, a sharp drop in pH or temperature can cause the hydrothermal fluid to become rapidly supersaturated with respect to silica (Fournier, 1985; Williams and Crerar, 1985). Theoretical modeling by Janecky and Seyfield (1984), suggests that quartz can deposit directly from high temperature (350°C) fluids by mixing with cool seawater. However, this is inconsistent with observations from the seafloor. The sluggish nucleation kinetics of quartz below 200°C inhibits precipitation from rapidly cooled fluids (Rimstidt and Barnes, 1980; Janecky and Seyfried, 1984). Alt et al. (1987) identified significant quartz in hydrothermal oxide deposits on seamounts near 21°N, East Pacific Rise. However, quartz there is a product of recrystallisation of amorphous silica in response to reheating within the growing sulfide deposit.

The formation of amorphous silica is facilitated by the presence of Fe-O-OH ions, which induce polymerisation of mutually repelling silica colloids or substrates in acid to neutral pH solutions (Williams and Crerar, 1985). Adsorption of silica by clays, iron oxides and other impurities can also remove silica from solution (Williams and Parks, 1985). In ironstones associated with pumice breccia, the high surface area of reactive glassy pumice fragments and shards may have provided nuclei for the precipitation of silica (and hematite) from the hydrothermal fluid (cf. Ohmoto et al., 1983). Early diagenetic minerals (e.g. clay, zeolite, hematite) were probably also present and promoted amorphous silica precipitation. In ironstone hosted by rhyolite and dacite, reaction of silica saturated fluids with glass may have promoted precipitation of hematite and silica. Ironstones with negative Ce anomalies suggest that precipitation of silica did not occur solely in response
to conductive cooling and that in addition, mixing with seawater or pore water was important.

Amorphous silica is relatively unstable and so readily transforms to more stable silica polymorphs (cristobalite, opal-CT, chalcedony or quartz). The time required for the transformations decreases as temperature increases and in the presence of solutions with high pH, high salinity or containing dissolved Mg (Fournier, 1985). In the Trooper Creek ironstones, preservation of pumice clasts and shards with delicate margins and vesicles implies replacement prior to significant compaction. This also suggests that the conversion of amorphous silica to quartz probably began early during the period of hydrothermal activity (cf. Renaut and Owen, 1988).

In many Trooper Creek Formation ironstones, the amorphous silica crystallised to form spherules (cf. Oehler 1976a,b). Coatings of iron minerals on the surface of some spherule types are interpreted to be due to surface adsorption effects or to exclusion of iron-rich impurities during spherule growth. Concentric bands of iron oxide were entrapped during growth. The bands provide evidence for the co-precipitation of iron oxide and silica or imply that hematite deposited first. In some cases, hematite acted as crystallisation nucleation centres. Similar textures have been recorded from some Precambrian ironstones (e.g. Oehler, 1976b). Oehler (1976b) demonstrated experimentally that chalcedonic spherules crystallise from a silica gel until the concentration of dissolved silica decreases below a critical value, following which, euhedral quartz crystallises from the remaining silica-depleted solution. In the Trooper Creek Formation ironstones, interlocking anhedral quartz which fills pore space in some ironstone samples may have deposited by the same mechanism. Botryoidal structures and nodules are interpreted to have grown at scattered nucleation sites (commonly feldspar crystals) within the amorphous silica gel.

Spherules originally comprised chalcedony (cf. Oehler, 1976b), but many progressively transformed to more stable quartz. Recrystallisation probably began early, but was most texturally destructive during metamorphism (cf. Duhig et al., 1992). Recrystallisation has destroyed or obscured radially fibrous textures of spherules, converting many to interlocking mosaics of anhedral quartz. In some cases, recrystallisation has not been pervasive and regions of quartz spherules grade into domains of interlocking anhedral quartz grains, and some spherules have only been partially converted to anhedral quartz.

At modern seafloor hydrothermal centres, Fe precipitates as iron oxyhydroxides (e.g. Hekinian and Fouquet, 1985; Alt et al., 1987; Holm, 1987). Hematite characterises some depositional settings (e.g. Soufrière volcano, Sigurdsson, 1977) and may have been the
primary oxide phase in the Trooper Creek ironstones. Alternatively, iron oxyhydroxide (e.g., goethite) may have formed an unstable precursor which later converted to more stable hematite. REE analysis and textures suggest that the Fe largely deposited at low temperatures and is consistent with studies of young deposits (e.g., Holm, 1987). At Santorini, Fe-oxidising bacteria in mud suggest that the iron-hydroxide deposited at 12-30°C (Holm, 1987). In the Trooper Creek Formation, ironstone lenses with filamentous algae/bacteria probably deposited at similar temperatures (cf. Duhig et al., 1992b). Syneresis cracks suggest that the oxide patches were more hydrated than the enclosing amorphous silica. In ironstone hosted by pumice breccia beds, fine-grained hematite delineates vesicle walls and pyroclast margin. As both vesicles and pumice/shard walls are now phyllosilicate or quartz, an early phase of hematite alteration is probably recorded. Cuspate patches of hematite between coalescing spherules probably deposited during and/or after growth of the spherules.

6.8.2 Evidence for sub-seafloor replacement

In the Trooper Creek Formation, relic pyroclasts suggest that some ironstone lenses formed by sub-seafloor replacement of pumice breccia units, or sedimentation was synchronous with hydrothermal activity and precipitation of iron and silica occurred at, above, and below the seafloor during ironstone deposition. Most of the iron and silica precipitated by sub-seafloor replacement and infiltration of pumice breccia because: (1) the ironstone lenses are hosted by rapidly or mass flow emplaced units (cf. Allen, 1994; chapter 7); (2) laminae within the pumice breccia units can be traced into the ironstone lenses; (3) there are replacement fronts passing from massive ironstone with rare pyroclasts, through tuffaceous ironstone, into hematite-altered pumice breccia with hematite-silica nodules; and (4) strong hematite alteration in siltstone beds which overlie some ironstone lenses, suggests that the hydrothermal activity continued during (and probably after) deposition of the siltstone units.

The distance below the seafloor at which infiltration and replacement occurred is difficult to interpret, but was not excessively deep because: (1) clasts of ironstone were incorporated into overlying subaqueous mass-flow deposits; and (2) the pumice breccia has been pervasively altered without producing veins. After lithification, alteration of pumiceous deposits is generally fracture controlled (McPhie et al., 1993).

The transition in mineralogy passing from massive ironstone (quartz-hematite), through tuffaceous ironstone (hematite>quartz), into pumice breccia (sericite>hematite), may record a decreasing involvement of hydrothermal fluids, in favour of diagenetic fluids,
during ironstone deposition. Alternatively, the ironstone lenses may mark the seawater mixing zone, whereas the hematite-sericite alteration may mark feeder zones within the sub-seafloor strata. Spherules are more abundant in massive ironstone compared to tuffaceous ironstone and hematite-altered pumice breccia. Massive ironstone may have deposited at, or near, the seafloor where the physical and chemical conditions promoted the growth of spherules. In tuffaceous ironstone and pumice breccia, early diagenetic compaction may have decreased the porosity and permeability and inhibited the growth of spherules in pumice breccia.

6.8.3 Role of micro-organisms in ironstone formation

Networks of filaments, similar to those described by Duhig et al. (1992a,b), are present in massive and tuffaceous ironstone, stromatolitic ironstone and in quartz-hematite veins in dacite. The filaments may be microaerophilic chemolithotrophic bacteria which were able to colonise sub-seafloor environments. The role of seafloor Fe-oxidising bacteria and algae in precipitation of iron oxide around hydrothermal vents is well documented (Trudinger and Mendelsohn, 1976; Holm 1987, 1989; Alt et al., 1987; Alt, 1988; Duhig et al., 1992b). Microaerophilic chemolithotrophic bacteria metabolise in oxygen-poor environments and are solely dependent on the immediate geochemical environment. The bacteria use energy liberated during the oxidation of Fe$^{2+}$ to Fe$^{3+}$ to secrete a mucus sheath composed of Fe-oxyhydroxides, which alter to more stable hematite during diagenesis. The recognition of filamentous structures in quartz-hematite veins supports the interpretation that microaerophilic chemolithotrophic organisms may be able to colonise sub-seafloor hydrothermal conduits (e.g. Haymon et al., 1993).

In the study area, microbial structures are rare, suggesting a limited role for micro-organisms in iron oxide deposition. Rather the microbial structures may have provided only a framework for iron oxide (or oxyhydroxide) minerals to deposit, and played no more direct role in mineral deposition than do crystal and vitric particles in the ironstone.

6.8.4 Palaeowater depths

In the study area, most ironstone lenses and pods are associated with volcanic and sedimentary facies which suggest a relatively deep (below storm wave base) submarine depositional setting (Chapters 3 and 5). The exception is at Trooper Creek prospect, where microbialites, gypsum molds, and traction current structures indicative of wave activity, imply that the ironstones accumulated above storm wave base (Chapter 4).
6.8.5 Models for ironstone emplacement

A spectrum of iron oxide deposit styles exist (Fig. 6.1), several of which depart from classic "blanket style" ironstone units associated with some massive sulfide deposits (e.g. Kalogeropulos and Scott, 1983, 1989). These differences reflect variation in the chemistry of hydrothermal fluids, different volcanic facies, the facies architecture and the character of the seafloor. In host successions to VHMS deposits, several different models have been proposed for iron oxide±silica units. Ironstones can record: (1) diffuse venting of hydrothermal fluids from white smoker chimneys and during the waxing and waning stages of massive sulfide deposition (e.g. Tivey and Delaney, 1986; Alt et al., 1987; Lydon, 1988; Hannington et al., 1995); (2) precipitation of oxyhydroxides by oxidation of sulfide particles in hydrothermal plumes above black smoker chimneys (e.g. Hannington et al., 1995; Lilley et al., 1995); (3) deposition of iron oxyhydroxides and silica from brine pools (e.g. Large, 1977; Pottorf and Barnes, 1983); or (4) sub-seafloor replacement of wet unconsolidated sediment by mixing of hydrothermal fluids and sea water (Ohmoto et al., 1983).

Other iron oxide±silica units are unrelated to massive sulfide mineralisation. The hydrothermal systems responsible for these iron oxide±silica units often operate in periods of heightened volcanic activity (e.g. Goodwin, 1962; Sigurdsson, 1977). During the 1971-72 eruption of Soufrière volcano, hematite-rich mud was deposited in the crater lake. Iron in the mud was interpreted to have been derived from convecting fluids which leached Fe and other elements from a glassy lava which partially filled the crater (Sigurdsson, 1977). Heat released from syn-sedimentary intrusions can also generate local hydrothermal systems capable of depositing iron oxyhydroxides on the seafloor (e.g. Einsele et al., 1980; Einsele, 1986).

Model for the Trooper Creek Formation ironstones

In the study area, the REE patterns of the iron oxide±silica units are generally distinct from ironstone lenses which forms the ore equivalent horizon at Thalanga. The iron oxide±silica units are regionally distributed and not preferentially associated with known mineralisation. The exception is two samples (94-18, 94-401) from Handcuff. These units have REE patterns similar to ironstone from Thalanga, have anomalous Ba, Zn, Pb and Ag, and may be associated with as yet undiscovered massive sulfide mineralisation.

The evidence suggests that most of the ironstone units are unrelated to massive sulfide mineralisation. At Trooper Creek prospect, iron oxide±silica deposition consistently followed the emplacement of syn-eruptive pumiceous deposits. The iron oxide±silica
units may record the establishment of shallow water hydrothermal systems following explosive eruptions at a nearby (unexposed/eroded) subaerial or shallow marine volcanic centre. Alternatively, they may be related to circulation of fluids around lavas/intrusions which occur within the succession. Other ironstone units are hosted by lava- and intrusion-dominated volcanic centres. These iron oxide-silica units occur along contacts with the enclosing strata, form the matrix in peperite, or occur as pods in the lavas or intrusions. This suggests that the iron oxide-silica units deposited during, after and prior to, emplacement of the associated lavas and intrusions. The spatial and temporal relationships of the iron oxide-silica units with the volcanic centres suggests that the hydrothermal systems may have been genetically related to the magmatism associated with emplacement of the lavas and intrusions. Convecting pore waters probably leached Fe and Si from the enclosing glassy volcanic succession and reprecipitated the Fe and Si by conductive cooling and mixing with seawater in the enclosing volcanic succession. Experimental studies show that volcanic glass readily contributes silica and iron to circulating hydrothermal solutions and feldspar is a source of Eu (e.g. Fournier, 1985). The absence of positive Eu anomalies in most iron oxide-silica units suggests that feldspar destruction was not important during leaching of the volcanic succession and/or that the host rocks were feldspar-poor. Most units in the Trooper Creek Formation contain feldspar, suggesting that the former was more important. Samples of ironstone with positive Eu anomalies were sourced from relatively hot fluids which leached feldspar-bearing volcanic rocks.

Many ironstone units are sub-seafloor replacements of pumice breccia and sandstone. Diffuse fluids which passed through the pumice breccia units, deposited amorphous Fe-Si-O-OH gel in pore space within the units and replaced glassy pyroclasts. It is possible that initial precipitation of hydrothermal minerals occurred at or near the seafloor, where sediments were more porous and contained greater seawater. An advancing Fe-Si-O-OH front progressively moved downward and laterally through the less altered parts of the pumice breccia units. The transformation of the amorphous gel into more stable silica and oxide minerals, probably began during replacement of the pumice breccia and may have also proceeded down from the seafloor. The quartz and hematite minerals may have formed a barrier to the ascending hydrothermal fluids. The low-permeability cap might have restricted circulation of mineralising fluids within the developing lenses, caused an upward migration of isotherms in the lenses, and so promoted the transformation of amorphous silica into more stable polymorphs (e.g. Oehler, 1976a,b). Siltstone which occurs above some iron oxide-silica units also acted as an aquitard. Hematite alteration extends into the siltstone, suggesting that fluids were able to penetrate these units. The thickness of some ironstone lenses suggests that the hydrothermal systems which deposited the iron and silica were long lived, that precipitation of minerals was very
efficient, and/or that large volumes of hydrothermal fluids passed through the pumice breccia units. Intense silica-hematite alteration of units beneath the ironstone lenses is interpreted to have deposited from diffuse fluids which passed through these units. There is evidence for topography on the original upper surface of the pumice breccia hosting horizon 1 ironstone. Rather than occupying the topographic lows, the ironstone lenses often replaced pumice breccia that mantled palaeotopographic highs, suggesting that the lenses did not accumulate from brine pools.

Selective replacement of permeable horizons by hydrothermal fluids may continue uninterrupted as younger deposits are emplaced from concurrent volcanic activity. The preservation potential of ironstones formed in this way may be higher than for exhalative deposits. On the seafloor, currents can disrupt and disperse exhaling hydrothermal fluids, and sediment gravity flows may erode poorly consolidated gels. The depth at which infiltration and replacement take place is poorly constrained. The upper few tens of metres may be the favoured position for replacement as sediments are wet and unconsolidated in this zone, and at greater depths become progressively more compacted (e.g. Einsele, 1986). The shapes, dimensions and viability of hydrothermal circulation, important for iron oxide-silica deposition, will be strongly dependent on the volcanic facies and their properties. This study suggests that distinct or genetically related iron oxide-silica deposits that involve different facies may contrast markedly in texture, structure and geochemistry.

6.9 Significance of ironstones to mineral exploration

Iron oxide-silica units occur throughout the Seventy Mile Range Group. Type 1 ironstones are characterised by positive Eu anomalies and anomalous Zn, Pb, Ba, Ag and Au. They are sourced from relatively high temperature, acidic and/or reduced hydrothermal fluids (cf. Duhig et al., 1992). Type 2 ironstones are characterised by negative Eu and Ce anomalies and contain little Ba, Pb or Zn (cf. Davidson et al., 1996). These ironstones deposit from oxidised, low temperature fluids which are in equilibrium with feldspar (alkaline/neutral). Type 1 ironstones are spatially associated with massive sulfide mineralisation (Fig. 6.19A). Type 2 ironstones are interpreted to deposit from low temperature fluids circulating around lavas and intrusions and within proximity to subaqueous explosive volcanoes (Fig. 6.19B).

As some styles of massive sulfide mineralisation are hosted in the proximal facies association submarine volcanic centres, type 2 ironstones are likely to be represented in these environments. This is the case at Highway-Reward. The Highway-Reward VHMS
Figure 6.19 Models for the formation of ironstone units in the Seventy Mile Range Group. (A) Type 1 ironstones are spatially associated with massive sulfide mineralisation and are sourced from reduced, high temperature fluids. They are vectors to mineralisation (cf. Duhig et al., 1992). (B) Barren (type 2) ironstones are not related to massive sulfide mineralisation. Type 2 ironstones deposit from oxidised, low temperature fluids circulating around volcanic centres. Type 2 ironstones can occur in the immediate host succession to massive sulfide mineralisation.
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deposit is hosted by a syn-sedimentary intrusion-dominated volcanic centre. Iron oxide-silica units and alteration occur in the host succession to mineralisation and are interpreted to have deposited from type 2 fluids related to the emplacement of the lavas and intrusions. At Handcuff, both type 1 and type 2 ironstone units are present. Type 2 ironstones are interpreted to have been emplaced from fluids circulating around lavas and intrusions which occur in the host succession. Type 1 ironstone units represent clear targets for further exploration.

6.10 Summary

Careful elucidation of the volcanic facies and facies architecture has proven to be critical in unravelling the exploration significance and emplacement processes of the iron oxide-silica rocks in the Trooper Creek Formation. The iron oxide-silica units occur as pods in lavas, domes and cryptodomes, and as lenses in pumiceous units and silicified siltstone. Hematite-quartz-carbonate also occurs as veins in coherent rhyolite and dacite, and as an alteration of the matrix in hyaloclastite and peperite.

Many of the iron oxide-silica units are interpreted to have been deposited from oxidised, alkaline, low temperature hydrothermal fluids, circulating around lavas and intrusions and within proximity to shallow submarine volcanoes. Convecting hydrothermal fluids leached Fe, Si and other elements from glassy volcanic deposits in the host succession, and reprecipitated the Fe and Si by conductive cooling and mixing with seawater in the enclosing volcanic package. Many iron oxide-silica units are sub-seafloor replacements of pumice breccia. The iron oxide-silica units are barren, characterised by negative Eu anomalies and distinct from ironstones that flank the massive sulfide mineralisation at Thalanga. At Handcuff, ironstone lenses with positive Eu anomalies and anomalous Pb, Zn, Ba and Ag are interpreted to have been sourced from relatively high temperature, reduced and acid hydrothermal fluids. These ironstone units are untested for massive sulfide mineralisation and are targets for exploration.