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ORE DEPOSIT TYPES AND THEIR PRIMARY EXPRESSIONS

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INTRODUCTION

Ore deposits are crustal concentrations of useful elements that can be exploited at a profit. Like all crustal rocks, they consist of minerals formed by geological processes. There are four basic geological requirements for any ore deposit to form (Figure 1): -

i) a source for the ore components (metals and ligands);

ii) a mechanism that either transports these components to the ore deposit site and allows the appropriate concentration or removes nonore components to allow residual concentration;

iii) a depositional mechanism (trap) to fix the components in the ore body as ore minerals and associated gangue;

iv) a process or geological setting that allows the ore deposit to be preserved.



Figure 1. The basic requirements for ore formation. The degree of element concentration during transport and deposition is a critical factor, but enriched sources can be important for reducing the required concentration factor and hence the required efficiency and probability of ore formation.

Additional and essential requirements include energy (generally thermal, gravitational or deformational) to power the transport mechanism and a suitable crustal structure to focus ore-forming components and accommodate their deposition.

Metals are largely derived from the mantle or crust by partial melting and fluid-related leaching. Ligands can be provided from the same sources, or from the atmosphere, hydrosphere and biosphere. Transport is mainly by mechanical or mass transfer mechanisms and by fluids. On and near the surface, biological processes can also concentrate and transport ore components or remove non-ore components. Hydrothermal fluids are a major transport medium for many ore systems; these fluids are essentially water, with lesser and variable amounts of CO₂, H₂S, SO₂, CH₄, N₂, NaCl and other salts, as well as dissolved metal complexes. They are derived from a variety of sources, including i) water-rich silicate melts, ii) circulated sea, connate and meteoric waters, iii) formational, diagenetic and metamorphic fluids. At upper crustal levels, the fluids are typically hotter than the rocks they traverse and in which they deposit their ores; they have variable pH and Eh, and they may be charged with a range of metal complexing agents including Cl⁻ and HS⁻. Deposition of ore minerals results from changes to physiochemical parameters, including temperature, pressure, pH, redox state and total concentration of ligands. These changes are associated with such processes as addition of components by contamination, phase separation, cooling across a temperature gradient, pressure decrease, fluid mixing and reaction with host rocks.

A large variety of geological processes can meet the essential requirements for ore deposit formation and the concentration of ore elements is best viewed as part of the geological (and geochemical) cycle. The vast array of ore deposit types and their particular elemental compositions result from the complex interplay of favourable combinations of source, transport and depositional variables. Although ore formation is a common and intrinsic part of crustal evolution, large

and super large ore deposits require the coincidence of particularly favourable combinations of processes and source parameters.

This brief review outlines the key primary geochemical expressions of the main metalliferous ore deposit types found in Australia. To a large extent, these expressions reflect ore-forming processes and are best described in reference to the different genetic ore types. There is now a large literature on Australian ore deposits, including their geochemical features (*e.g.*, Knight, 1975; Hughes, 1990; Berkman and Mackenzie, 1998; AGSO Journal, 1998; Solomon and Groves, 2000; Jaques *et al.*, 2002).

ORE DEPOSIT TYPES

Ore deposits can be classified on the basis of: -

- Composition of the deposit (contained elements).
- Form of the deposit (size, shape, orientation and ore mineral distribution).
- Associated host rocks or geological structures (ore associations).
- Interpreted genesis of the deposit (processes, controls).

Geologists generally prefer genetic classification schemes that also incorporate elements of composition, form and association. From these, it is possible to construct predictive models that can be used to search for geological environments in which appropriate ore-forming processes have probably operated. Increasing knowledge of planetary evolution and the global plate tectonic system now provides a better understanding of the context of ore-forming geological environments and processes. A number of major metallogenic epochs are recognized and these are thought to relate to global geodynamic processes, including major periods of crustal break-up and convergence (*e.g.*, Jaques *et al.*, 2002).

A simplified genetic classification encompassing all ore deposit types is shown in Figure 2. This scheme highlights the broad categories of oreforming processes and the later overprints that may affect the deposits. Deposits can also be broadly subdivided into syngenetic (formed with the enclosing rocks) and epigenetic (introduced into pre-existing rocks). Deposit form and geometry can vary greatly but, in many cases, these features also reflect the nature of the ore-forming process. Thus, hydrothermal deposits show forms related to the geometry of the fluid channelways (*e.g.*, veins or stockworks along fractures). Syngenetic deposits are commonly stratabound (*i.e.*, confined to a particular stratigraphic layer or unit) or stratiform (*i.e.*, confined to the stratigraphy and internally stratified or layered). Examples of deposit types related to the major groups of ore-forming processes are given in Table 1.

For geochemical detection, the composition, size and geometry of ore deposits and any related distribution pattern of associated elements or



Figure 2. A simplified genetic classification scheme for ore deposits showing the major groups of ore-forming and modifying processes.

TABLE 1

AUSTRALIAN ORE DEPOSIT TYPES WITH TYPICAL ELEMENT ASSOCIATIONS

Ore Group	Some Deposit Types and Examples	I ypical Element Associations*
Magmatic	Komatiite-associated nickel deposits	
	Mt Keith, Kambalda, Widgiemooltha, Maggie Hays, Jubilee.	NI-Cu-Co-PGE±Te (S) minor As
	Layered mafic-ultramafic intrusion deposits	
	PGE sulphide and chromite deposits: Munni Munni, Ora Banda, Yarawindah.	Cr-PGE-Ni-Cu-Co-Au (S-O)
	Vanadiferous magnetite: Windimurra.	Fe-Ti-V (O)
Metasomatic	Skarn deposits	
	Copper-gold skarns: Browns Creek, Big Cadia, Red Dome.	Cu-Au-Bi-Te (S)
	Distal gold skarns: Junction Reefs.	Au-As-Bi-Te (S)
	Magnetite skarns: Biggenden.	Fe-Cu-Pb-Zn-Ag (S)
	Zinc-lead-copper skarns: Ban Ban.	Zn-Pb-Cu-As-Ag (S)
	Tungsten skarns: King Island.	W-Mo±Cu-Pb-Zn (O,S)
Hydrothermal	Fractionated granitoid-associated deposits	
epigenetic	Tin-tungsten deposits: Mt Bischoff, Renison, Ardlethan.	Sn-W±As-Cu-Zn (O-S-F-B)
	Tungsten-molybdenum deposits: Wolfram Camp.	W-Mo±Cu-Pb-Zn-Bi-As
	Pegmatite and complex veins: Greenbushes, Wodgina.	Sn-Ta-Nb-Li, Be-Li-Cs-Rb±U-Th REE (Si)
	Porphyry-associated deposits	
	Copper-gold stockworks and veins: Cadia-Ridgeway, Northparkes,	Cu-Au±Ag-Bi-Mo-Te-Re (S-K)
	Copper Hill.	
	Copper-molybdenum deposits: Dogwood.	Mo-Cu (S)
	Breccia pipe deposits: Kidston, Mt Levshon.	Au±Cu-Ag±Mo-Pb-Zn (S)
	Epithermal gold-silver deposits:	
	High sulphidation type: <i>Peak Hill</i> , Gidginbung.	Aa-Au-As-Sb-Te (S-Si)
	Low sulphidation type: <i>Paiingo</i> .	Ag-Au-As-Sb-Mn-Ba±Hg-Te-Se (S-Si-CO ₂)
	Iron oxide copper gold deposits	
	Olympic Dam. Ernest Henry.	Cu-U-Au-Aa-REE (S-F)
	Tennant Creek.	Cu-Au-Bi
	Syn-deformational hydrothermal and replacement deposits	
	Metamorphic copper denosite: Mount Isa Nifty	$Cu_{-}Co_{-}As_{+}Pb_{-}Zn_{-}(S_{-}Si)$
	Metanolphic copper deposits. <i>Mount isa</i> , <i>Ninty</i> .	$Pb_7n_4a_+CuSb(S)$
	CSA Book Now Cobor Hore Tritton	$C_{11} - A_{11} + B_{1} - A_{0} - B_{0} - Z_{0} $
	CSA, Peak, New Cobar, Hera, Thilon.	$Gu Au \pm Di - AS - F D - Z II (S)$
		Gu-Au-Ag-Bi-Go-Hg-100-3e-311-1e-10 (3-F)±211-Fb
	Orogenic gold deposits	An An An M/ Ch Tai Cu Ph Ma (CO Cull D)
	Archaean greenstone-nosted deposits: Eastern Goldfields, WA (e.g., Golden	Au-Ag-As-w-Sb-Te \pm Cu-Pb-Mo (CO $_2$ -S \pm K-B)
	Mile, Mt Charlotte, Bronzewing, Junction, Kanowna Belle, Bounty);	
	Sediment-hosted reef deposits: Telfer.	
	Slate-hosted quartz-vein deposits: Central Victoria, Hill End.	Au-As-Sb \pm Ag (CO ₂ -S)
	Granitoid-associated deposits: Charters Towers, Timbarra.	Au-Ag-Zn-Pb-Cu-Bi (CO ₂ -S)
	Carbonate-hosted stratabound lead-zinc deposits	
	Mississippi Valley-type: Lennard Shelf.	Pb-Zn-Fe±Ag-Cu (S-hydrocarbons)
	Unconformity-related uranium deposits	
	Alligator River, Coronation Hill.	U-Au-Cu-Co-Ni-Ag±Zn-Sn-Pb-Bi, Pt-Pd (Mg)
Exhalative	Volcanic-associated massive sulphide deposits	
- diagenetic	Abitibi type: Scuddles, Gossan Hill, Teutonic Bore, Sulphur Springs,	Cu-Zn-Pb±As-Sb-Bi-Sn-Mo-Se-Ag-Au-Ba (S)
	Mons Cupri, Whim Creek.	
	Kuroko type: Mt Lyell, Rosebery, Hellyer, Hercules, Woodlawn,	Pb-Zn-Ag±As-Sb-Hg-Ba, Cu±Bi-Sn-Te-Mo-Co-Au
	Captains Flat, Thalanga, Balcooma, Mt Morgan, Halls Peak.	(S), Cu-Au-Ag-Zn-Te
	Sediment-hosted stratiform base metal deposits	
	HYC, Mount Isa (lead-zinc), Century, Broken Hill.	Zn-Pb-Ag-Cd-Mn-Ba-Tl±Cu-As-Sb-Hg-In (S-K-B)
	Sediment hosted copper deposits	
	Sandstone-hosted: Mt Gunson, Cattle Grid.	Cu-Zn-Pb-Bi-Co-Ni-As±Ag-Au (S)
Marine	Banded iron formations (generally precursor ores)	
-sedimentary	Hamersley Range, Middleback Ranges.	Fe-Mg-Al-Ca-Mn-P±Ti (Si-O-S)
	Sedimentary manganese deposits	
	Groote Eylandt.	Mn-Fe±Ca-Al-Zn-Li-Ba (O-Si-CO ₂)
Residual &	Bauxite deposits	
supergene	Gove, Weipa, Jarrahdale, Mitchell Plateau.	AI-Fe±11-Nb-Ga-Min-Zn-Zr (O)
	Lateritic nickel-cobalt deposits	
	Murrin Murrin, Cawse, Bulong, Greenvale.	Fe-Ni±Co-Mn-Cr-Zn (Si-O)
	Lateritic & supergene gold deposits	
	Deposits in thick regolith; e.g., Mt Gibson, Boddington, Panglo, McKinnons.	Au±Ag-As-W-Sb-Bi (lateritic types)
	Supergene deposits associated with palaeochannels	A
	Higginsville, Mount Pleasant, Zuleika.	Au
	Lateritic phosphate-REE-ND deposits	
		P-REE-ND±Sr-Ga-Al-K-U-11-1a
	Supergene iron ores & transported channel deposits	Fa Mau D
	Mt Whaleback, Paraburdoo, Iron Duke, Robe River.	Fe-Min±P
	Teenime.	υ-ν (Γ -υU ₂)
	Reduced palaeocnannel/"roll front" uranium deposits	
Disc	Iviuiga HOCK, Manyingee	U±5-AS-5e-MO-CO-NI-V-CU-ZN-PD-KEE-Y (SI-O-C-P)
Placers	Placer gold deposits	
	Central VICtoria, Kanowna (?)	Au-Ag±w-11-∠r-ba
	Heavy mineral sand deposits	
	Central E and W coasts, Murray Basin.	II-Fe-Zr-IN-KEE±Cr-Sn
	Placer tin deposits	
1	I Emmaville Ardlethan	I Sn-Fe-Ti+W-Nb-Ta

*Fe is a significant component in most sulphide-bearing deposits generally in abundant pyrite/pyrrhotite but also in other minerals (elements and compounds in parentheses are characteristic and significant non metallic components/additions) Deposit examples described in case histories shown in italics: e.g., *Mt Keith* wall-rock alteration are key features. Typical element associations for a range of deposit types are listed in Table 1. Some of the elements in these associations are not the direct target of exploration and discovery, but they can provide very useful pathfinders to the deposit.

PRIMARY EXPRESSIONS OF ORE DEPOSITS

A well known aspect of ore deposit expression is the association of particular ore types with particular host rock assemblages, *i.e.*, the orehost rock association (*e.g.*, Stanton, 1972). This association broadly reflects the geological environment and processes that have formed the ore. Identified associations have been widely and successfully used in an empirical approach to the search for new deposits. The ore and associated minerals in ore deposits comprise rocks that may be significantly different in their physical and chemical properties from the enclosing host rocks. Distinct physical properties such as density, magnetic characteristics, radiometric signatures and electrical properties can provide a detectable geophysical expression. Silicification and other types of induration can result in a positive topographic expression following differential erosion.

From a geochemical point of view, ore deposits represent anomalous crustal accumulations of particular elements. They typically show multi-element enrichments and depletions relative to their enclosing host rocks. These anomalies extend beyond the limits of the deposit to varying degrees to form a geochemical dispersion halo. This pattern or halo can be formed at or close to the time of ore formation (syndepositional) or subsequently when the ore deposit is weathered (postdepositional). The former is a primary dispersion pattern, as for most deposits this forms in the primary environment (i.e., below the weathering front). The latter is a secondary dispersion pattern as it is generally formed in the near surface secondary environment by weathering, erosion and hydrological processes (Figure 3). Some types of ore deposits form in the secondary environment and then undergo later weathering so that they may have syn-depositional and post-depositional patterns that have both formed in the secondary environment (e.g., residual, supergene and placer deposits).

Primary dispersion patterns include two components: -

- The sub-ore grade portion of the deposit (ore deposits are defined by an economic minimum cut-off grade for the ore elements);
- The enclosing or related zones of non-ore element enrichment or depletion.

The non-ore element component of the primary ore expression can be more extensive and obvious than the dispersed ore elements. It may be expressed by extensive fluid-related alteration of the host rocks including silicification, pyritization, sericitization, chloritization carbonate alteration, tourmalinization or development of greisens. Other primary geochemical features include spatial and temporal zoning of contained elements and alteration types, particular isotopic characteristics and compositional variation in fluids trapped in fluid inclusions. Mineralizing fluids that have escaped the immediate ore



Figure 3. The generalized occurrence and possible relationships between primary and secondary geochemical dispersion patterns around ore deposits.

depositional environment and significantly penetrated structural or permeability channelways can produce distal leakage anomalies (Figure 3).

The mineralogical changes associated with the formation or emplacement of mineralization, such as those expressed by hydrothermal alteration haloes, are a significant component of the primary dispersion pattern. Rapid radiometric and, especially, hyperspectral analyses that permit mapping of key minerals by airborne and ground surveys, and automated logging of drill cuttings and core of fresh and weathered rocks, are playing an increasingly important role in exploration, especially in covered terrain.

Correctly identifying primary dispersion patterns around major ore systems as distinct from around bodies of low-grade or non-economic mineralization is critical in exploration. Also, it is sobering to reflect on the possible number of disregarded drill intersections of low-grade mineralization that may have been primary dispersion from undiscovered ore deposits.

The extent, shape and intensity of primary dispersion patterns are a function of the ore-forming process (including the physico-chemical conditions prevailing during transport and deposition), nature of the host rocks and types of controlling structures. Typical patterns are best described in terms of the major ore-forming processes and ore deposit types.

DISPERSION AROUND MAGMATIC DEPOSITS

Magmatic ore formation involves crystallization or exsolution of ore minerals from a silicate melt or associated sulphide-oxide phase, with separation and concentration of the ore minerals or immiscible phases by a suitable mechanism such as gravity settling, filter pressing, convective accumulation or dynamic flow. Sulphide immiscibility and monomineralic oxide crystallization can be caused by contamination of magmas with crustal sulphur, mixing of magmas or contamination with felsic crust, combined with processes accompanying fractional crystallization.

Magmatic dispersion patterns typically involve decreasing concentrations of the ore minerals above or peripheral to the main deposit, reflecting incomplete separation of the ore minerals from the magma or other crystalline components. In some cases, the dispersion of ore minerals may be very localized. Magmatic Ni-Cu sulphide deposits commonly have a halo of disseminated sulphides around massive or semi-massive ore, particularly in the hanging-wall. High background S abundances can indicate S-saturation of a particular unit and hence the possibility of immiscible sulphide development and ore formation. Mineralized mafic intrusions commonly show evidence of magma mixing or magma contamination by silica-rich crustal material or crustal S (e.g., Campbell et al., 1983; Naldrett, 1989; 1997). Multistage magma emplacement may also lead to partial or complete sulphide re-dissolution with complicating effects for element distribution patterns (including possible metal upgrading of residual sulphide, Kerr and Leitch, 2005).

Styles of mineralization in layered mafic and ultramafic intrusions in Australia include stratabound layers of disseminated Ni-Cu sulphides enriched in PGEs, stratabound chromitite layers (in some cases, such as the Panton Sill in the Halls Creek orogen, with PGE-rich sulphides) and basal segregations of Ni-Cu-Co-PGE sulphides (Hoatson, 1998). Stratabound sulphide layers can be of great lateral extent, but are thin (<3 m) and difficult to detect in the larger body of the host intrusion (Hoatson, 1998). Sulphur and Cr concentrations can be useful indicators of potentially mineralized intrusions. Marked discontinuities in stratigraphic profiles of S, Cu, (Pt+Pd)/Cu, (Pt+Pd)/S, (Pt+Pd)/Zr, (Pt+Pd)/Ir, Pt/Pd, Cu/Zr and Mg/(Mg+Fe) may indicate mixing of magma pulses, onset of S saturation and mineralized layers (Hoatson and Keays, 1989).

Sulphides in komatiite-hosted Ni deposits are believed to have formed by thermomechanical erosion of sulphide-bearing substrates at the base of lava tubes (Figure 4; Lesher, 1989). Substrate xenoliths and xenomelts in ores (Dowling *et al.*, 2004) and major element anomalies in host rocks (*e.g.*, elevated LREE, Zr and Y) are indicators of



Figure 4. Schematic cross-section of an evolving komatilite flow field, illustrating the process of thermo-mechanical erosion of sulphidic substrate at the base of a preferred lava pathway and the formation of Type I Ni deposits and their primary dispersion features (after Hill, 2001).

contamination processes related to mineralization. Where the substrate is predominantly mafic, the signatures are very subtle (Lesher et al., 2001; Barnes et al., 2004b). Some mineralized komatiite flows contain Zn-rich spinel phases, which have been regarded as indicators of mineralization potential (Groves et al., 1983); however, it has since been shown that Zn enrichment in spinel is largely the consequence of introduction during alteration (Barnes, 2000). Units hosting major Ni-Cu sulphide mineralization may also show depletion of chalcophile elements and PGEs due to their scavenging and removal from the silicate liquid by sulphides (Barnes et al., 1995; Lesher et al., 2001). This signature is not always present, and most komatiites (even those hosting mineralization) were evidently erupted S-undersaturated and undepleted in PGEs (Barnes et al., 2004b; Barnes et al., 2004a). Elevated Ni:Cr ratios are indicative of favourable environments for mineralization (Barnes and Brand, 1999), and vice versa. However, the only reliable lithogeochemical indicator is the presence of a halo of low-grade disseminated sulphides, the best indicator of which is Ni elevated above the expected linear Ni-MgO trend found in komatiites. The application of element ratios in discriminating gossans derived from Ni sulphides from other ironstones, and in providing vectors towards ore is discussed in Sample Media (this volume).

DISPERSION AROUND CONTACT METASOMATIC (SKARN) DEPOSITS

Contact metasomatism involves fluid-assisted diffusion and transfer of elements between volatile-bearing intrusions and reactive country rock (particularly carbonate-rich and mafic volcanic rocks). The resulting contact metasomatic rocks or skarns can host deposits of magnetite, Cu, Pb-Zn, Sn, W, Mo, Au, Ag, U, REE, F, B and Sn (Einaudi et al., 1981). Element transfer can occur in both directions to produce exoskarns (altered country rock) and endoskarns (altered intrusive phase). Fluid activity occurs at prograde and retrograde stages, with fluids derived from the intruded pluton and the country rocks. The prograde stage typically involves major addition of Si, Fe, alkalis, F and B to produce distinctive skarn silicate assemblages that show an outward zonation of anhydrous and hydrous phases. Common minerals in the inner skarn zone of calcic skarns are garnets (commonly grossularite and andradite), pyroxenes (typically diopside and hedenbergite), followed by wollastonite and other pyroxenoids, with surrounding and partly overprinting amphibole-, chlorite- and epidote/vesuvianite-bearing assemblages and clays. In aluminous host rocks, biotite, garnets, cordierite, gedrite and andalusite are common in the prograde inner hornfelsed zone. Much of the metal sulphide and gold mineralization is typically introduced at the retrograde stage by late-stage fluids, derived, in some cases, by ingress of connate water (e.g., Meinert, 1998). This mineralization is, thus, commonly associated with overprinting and hydrous mineral phases.

Skarns are a highly variable class of deposit and the mineralogy and primary geochemical expression of individual skarns differ significantly. Generally, there is no consistent enrichment of ore elements in the



Figure 5. Schematic structure of skarn deposits showing typical alteration mineralogy and metal zoning.

parent intrusion, so primary dispersion patterns are confined to the surrounding country rocks. These patterns are commonly very irregular and highly dependent on variation in the mobility of elements as a function of lithology and changes in redox conditions, temperature and pressure. Fluids that access favourable structures may move considerable distances to reactive sites to form distal skarns or they may develop minor hydrothermal vein infillings. Recognition of element distributions and skarn mineral zoning is an important method of vectoring towards mineralization in skarn systems (Figure 5). In reduced high to low temperature polymetallic systems, metal zoning commonly follows a pattern of Cu-(Au-W-Mo) to Cu-Zn-(Ag) to Zn-Pb-Ag to Pb-Ag to Mn-Ag to Mn to Hg from the inner to the distal parts of the system (Megaw, 1998). As a result, ratios of Zn/Cu and Pb/Cu commonly increase outwards. Gold skarns typically show an association of Au-As-Bi-Te, generally with base metals (particularly Cu), consistent with Au transport in saline and hypersaline fluids. Where the host rocks are impure limestones or contain a significant shale component, there may be enclosing biotite±K-feldspar alteration (Meinert, 1998). This potassic alteration is probably related to release of K from the inner skarn zone, as well as addition of K from the host pluton.

DISPERSION ASSOCIATED WITH HYDROTHERMAL DEPOSITS

Hydrothermal ore deposits can be broadly divided into: -

- vein or stockwork systems, in which solutions have deposited ore minerals in brittle structures or cavities;
- replacement deposits in which solutions have reacted with host rocks, leading to replacement of silicates and carbonates by new gangue and ore minerals.

These two forms can overlap or merge in some systems. For example, some Au deposits have mineralized alteration zones around distinct structurally-controlled veins.

Primary dispersion patterns associated with these types of deposits are largely related to the movement of hydrothermal fluids through the host rocks. Element transfer to the host rocks can be by fluid-related diffusion (and fluid-wall rock reaction), fluid flow through fractures and pore spaces, or a combination of these processes. Patterns of element distribution along the fluid path reflect temperature and pressure changes, and progressive reaction with the wall rocks or intermixed fluid (*e.g.*, meteoric fluids of different pH, Eh, composition and temperature). The nature and extent of primary dispersion also varies with the style of hydrothermal mineralization.

Vein-type deposits commonly have a strong, narrow pattern of anomalous abundances of ore elements in the wall rocks close to mineralization, with a logarithmic reduction away from the vein. This reflects element diffusion which, in some cases, is restricted to a few metres and rarely extends more than 50 m (Figure 6). The permeability and reactivity of the host rock to the ore fluid affect the width of the dispersion pattern. If the host rock is very reactive, the dispersion may be limited (e.g., particularly for acid fluids encountering carbonate rocks where metal complex solubility and hence element mobility may be limited by increased pH). If the host rocks are very permeable or strongly fractured and not particularly reactive, fluids may carry elements further from the main conduit before deposition, giving a broader primary dispersion halo. Wall rock alteration, particularly silicification, can cause sealing of the fluid conduit system restricting further fluid dispersion unless there is ongoing brittle fracturing. Veinrelated dispersion patterns can thus be generalized as being extensive along the vein systems, but of limited extent away from the veins. Large hydrothermal vein systems may exhibit element zoning along the veins (i.e., axial zoning, typically in a vertical sense if the veins are steeply dipping). This is related to changes in physio-chemical parameters (particularly temperature and fluid composition) along the fluid flow path. Patterns in element associations reflecting proximal versus distal conditions have been used in an empirical way to predict ore body locations (e.g., Beus and Grigorian, 1977).



Figure 6. Typical primary dispersion around a hydrothermal vein system. Controlling factors are fluid composition, pH, Eh, wall rock reactivity relative to fluid, wall rock permeability and fluid pressure (vs hydrostatic and lithostatic). Graphs show theoretical shapes of dispersion patterns for diffusion and infiltration mechanisms (after Rose et al., 1979).

Large-scale movement of hydrothermal fluids along extensive fault and fracture systems (as distinct from diffusion through rock and small fractures) can cause widespread leakage geochemical anomalies around vein systems. Regional-scale element dispersion has been documented around major hydrothermal systems (e.g., extending up to 8 km for Ag, Te, Sb, As, Pb, S and Cd in the Coeur d'Alene district of Idaho, USA; Govett, 1983). Some vein systems also show metal zonation on a district or regional scale, related to different stages and conditions of deposition. Well-described examples include the concentric outward zonation of Sn, Cu, Pb-Zn and Fe-Sb sulphosalt mineralization in and around granites of the Cornubian Batholith in Cornwall, UK (Guilbert and Park, 1986). Vein deposits in the Zeehan district of Tasmania and around the Mole Granite in northern NSW show similar depositional zoning (Solomon and Groves, 2000). At Zeehan, carbonate-replacement style sulphide-rich Sn mineralization is surrounded by Ag-bearing galena-sphalerite veins. In and around the Mole Granite, there are different stages of mineralization related to early high temperature pegmatites, followed by Sn-W veins and later sheeted vein systems with mixed Sn, Bi and base metal sulphide mineralization.

Disseminated stockwork and replacement deposits commonly show an envelope of weak mineralization around the ore, giving a larger dispersion pattern and exploration target. Porphyry-hosted deposits typically have a well-developed fracture network ('crackle breccia') required to facilitate fluid movement. These fractures may persist beyond the limit of major mineralization. The inner zones of porphyry systems are enriched in K and depleted in Ca and Mg, due to potassic alteration and the breakdown of plagioclase and hornblende. Porphyry Cu deposits show extensive Cu and S (as sulphide) anomalies (commonly extending 500-1000 m around the mineralized porphyry zone). Metal zoning is also commonly present. Copper is concentrated in the inner zones (although there may be a low-Cu core), decreasing outwards to the periphery of the system, where Zn and Mn abundances are elevated. Ore mineral zoning is also common. For example, the Northparkes and Cadia-Ridgeway porphyry Cu-Au deposits in central NSW show zoning from bornite-dominated cores to chalcopyritedominated outer zones and irregularly developed marginal pyritedominated zones. In these systems, an increasing bornite/chalcopyrite ratio can be used as a vector to higher grade cores (Smith *et al.*, 2004). Gold in these deposits is mostly associated with bornite and at Cadia Hill with chalcopyrite. Other associated elements in porphyry systems include Mo, Ag, Pb, As, Sb, Te and Sn, depending on the style of system.



Figure 7. Summary of spatial and temporal wall rock alteration patterns around porphyry copper-gold systems, also showing key alteration minerals and distribution of major sulphides in the mineralized stockwork (adapted from Wilson et al., 2003; Corbett, 2004).

Wall rock alteration, involving major element changes, is common in hydrothermal deposits, particularly where the hydrothermal fluids are significantly out of equilibrium with the enclosing rocks. These alteration patterns have been extensively studied and described for porphyry Cu and epithermal Au-Ag systems. Porphyry deposits commonly have a zoned pattern of alteration (Figure 7). Where expressed fully, this pattern consists of an inner zone of K alteration, with quartz - K-feldspar-biotite, grading out into a zone of phyllic alteration, with quartz-sericite (fine-grained muscovite) and an outer zone of propylitic alteration (chlorite-epidote-carbonate assemblages) (Figure 7). This alteration reflects relative enrichment in K (and Rb) in the inner zones and high Ca (and Sr) in the propylitic zone, with accompanying volatile enrichment. The patterns are not always as well defined and, in many systems where there have been multiple stages of porphyry and dyke intrusion, there is superposition of different styles of alteration at different stages of deposit evolution. The Northparkes deposits show a series of partly superimposed alteration stages. There is an early biotite-magnetite and propylitic alteration of the host volcanic rocks, followed by a main stage, magnetitedestructive potassic alteration (K-feldspar and sericite-hematite), a late sericite alteration and, finally, weak to moderate propylitic alteration (Heithersay and Walshe, 1995; Lickfold et al., 2003). Alteration is restricted to within 750 m of the core of the deposit and occurs in both the intrusive and surrounding volcanic rocks. At the Cadia-Ridgeway deposits, magnetite veining and alteration with some K-feldspar and biotite occurred with emplacement of early intrusions. This was followed by calc-potassic (actinolite-biotite-magnetite-apatite) or potassic alteration (orthoclase dominant), which accompanied the main ore stage (Wilson et al., 2003). Propylitic and sodic (albite-bearing) alteration zones occur peripheral to and locally overprint the potassic alteration. There is also some phyllic (sericite-rich) alteration restricted to late faults. At the Ridgeway deposit, the central calc-potassic alteration extends for 150 m, the surrounding potassic alteration for

a further 300 m and the propylitic alteration (chlorite-albite-pyriteepidote) for at least 600 m (Wilson *et al.*, 2003). Hematite dusting is also a feature of the altered intrusions and host volcanic rocks in deposits in central NSW, colouring the rocks a distinct pink-orange.

Epithermal systems can be divided into two main types, each with its characteristic mineralogy and wall-rock alteration (Figure 8). The two types are: -

i) High sulphidation systems, formed from oxidized acidic fluids generated in the magmatic hydrothermal environment.

ii) Low sulphidation systems formed from reduced, near-neutral fluids with a large input of meteoric water.



Figure 8. Summary of typical contrasting alteration patterns and fluid processes related to low sulphidation and high sulphidation epithermal systems (from White and Hedenquist, 1995).

In *high sulphidation* systems, SO₂- and HCl-rich vapour is absorbed by near-surface waters, causing SO₂ to disproportionate into H_2SO_4 and H_2S . The highly acidic fluids (pH 0-2) react extensively with, and leach, the host rock at shallow depth. This produces intense argillic alteration (kaolinite, dickite, pyrophyllite, diaspore and alunite), which passes outwards into argillic alteration with less clay and increased illite or smectite, and finally to an outer zone of propylitic alteration (albite, calcite, chlorite, epidote). The acidic water is progressively neutralized by the host rock, away from the conduits (White and Hedenquist, 1995). Mineralization occurs in a silicified core or vein system of microcrystalline (chalcedonic) quartz with disseminated and veinlet sulphides.

In *low sulphidation* systems, CO_2 , H_2S and NaCl are the main fluid species. Boiling around the ore zone causes loss of CO_2 and H_2S and a consequent increase in pH. The high-pH fluids deposit calcite and adularia. Clays are formed around the system with illite at depth (in the hotter parts) and interlayered illite-smectite followed by smectite in the upper and cooler parts. Other associated minerals include zeolites (at low temperature) and epidote (at higher temperature). Hydrothermal biotite and amphiboles may form above 280°C. Mineralization commonly occurs in well-defined vuggy veins with amethystine quartz.

Many hydrothermal ore deposits have formed during orogenesis and their genesis is directly related to episodes of deformation that preceded, accompanied or followed regional metamorphism. These include syn-deformational hydrothermal sulphide deposits that consist of structurally-controlled and stratabound vein zones and networks in variably altered and replaced metasedimentary rocks. The mineralized vein networks and associated hydrothermal breccias commonly occupy pipe-shaped or lobate bodies of alteration and were deposited from evolving fluids apparently related to large-scale dewatering and metamorphic processes. The Mt Isa Cu ore bodies are examples of this type of deposit (Perkins, 1984). They occur in silicified dolomitic shales adjacent to pyritic stratiform mineralization, and formed from ore fluids introduced during continuous deformation at or after the peak of regional metamorphism. Introduced components include Cu, Co, As, S, Fe, Si and Mg, with accompanying relative depletion of Zn, Pb, K, Al and Ca (Waring et al., 1998). The main associated alteration is silicification of the dolomitic host to produce a distinctive silica-dolomite rock. A zone of sparse dolomite veining with variable amounts of chalcopyrite encloses the silica-dolomite. Copper grade increases with the intensity of silicification. Strong depletion in ¹⁸O, related to large scale fluid interaction with the host rocks, has been documented around the Mt Isa Cu ores, and forms a halo more than 2 km across in dolomite showing no visible alteration (Waring *et al.*, 1998).

Metasediment-hosted polymetallic vein and replacement deposits, in the deformed Cobar Basin in western NSW, are another type of syndeformational hydrothermal sulphide deposit. These deposits occur along major fault and shear zones commonly within dilations related to competency contrasts. Individual deposits have characteristic metal contents and show overprinted element associations related to different stages of fluid flow and deposition (Stegman 2001). There is some evidence of vertical zonation (e.g., increase in Zn-Pb-Cu and decrease in Ag-As with depth at the Elura deposit and increase in Cu with depth in the CSA ore bodies). There are differences in metal ratios for different deposits along major structures: for example, Au-rich, Cu-Au, Cu and Au-Cu-Pb-Zn deposits occur along the Chesney Fault zone. There is also a regional scale (over 50 km) metal zonation of deposits along the eastern margin of the Cobar Basin, marked by increasing Ag-Pb-Zn and decreasing Cu-Au from S to N. Other trace elements variably associated with the deposits include As, Sb, Bi, Ni, Cd, Hg, Sn, Ba and, possibly, REE. Strong silicification occurs proximal (generally within 20 m) to the ore and is accompanied by chlorite and quartz-carbonate veining and the formation of sericite, albite and stilpnomelane. There may be an outer envelope of alteration (extending for several hundred metres) characterized by alteration of illite (to muscovite), and destruction of albite together with, at Elura, spotty carbonate (siderite-ankerite) alteration. In some cases, primary chlorite may also be destroyed or is absent in this alteration envelope. Black chlorite is commonly developed along late-stage faults in the deposits.

Orogenic gold deposits have typically formed from reduced, near neutral, CO,-rich and H,S-bearing fluids of low salinity. It is widely accepted that Au was transported as Au(HS),⁻ in such fluids, and that deposition involved reaction of the fluids with Fe in suitable host rocks to form pyrite and assist destabilization of the Au-bearing complex. These deposits include alteration lode and vein style mineralization deposited in brittle-ductile structures synchronous with deformation. They are commonly referred to as 'Au only' deposits, highlighting their low base metal content, due to the preference for 'soft' ion bonding by the transporting bisulphide complex. The ores typically have an association of Au-Ag-As-W-Sb-Te, with variable Cu-Pb-Bi-Mo-Zn. Pyrite (or pyrrhotite in high-grade metamorphic terrains) and arsenopyrite are the main associated sulphide minerals and commonly form a broad mineralized halo. Elements that show useful primary dispersion (up to 200 m) include As (hosted in dispersed pyrite or arsenopyrite) and, to a lesser extent, Sb, Te, W and Au, as well as Cu, Zn and Ba where these are significant in the ore. The fluids involved in these systems produce characteristic wall rock alteration that includes formation of Fe sulphides, carbonate alteration and K±Na metasomatism. In Archaean greenstone-hosted deposits, the nature of the alteration varies according to host rock and metamorphic grade (Figure 9; Yeats and Vanderhor, 1998). In mafic rocks at low metamorphic grade, the typical alteration is carbonate (ankerite, dolomite, siderite)-sericite-pyrite-pyrrhotite adjacent to mineralization, grading to distal chlorite-carbonate (calcite) alteration. The zone of alteration may also contain Si-Fe-Mg- (phengitic), V- and Cr-rich micas. In higher metamorphic grade terrains, biotite becomes prominent in the intermediate alteration zone and sericite is much less abundant. In *ultramafic* host rocks, the same chemical zonation involves highly magnesian minerals such as talc and tremolite. In high-grade metamorphic terrains, the chemical alteration of the typical maficultramafic host rocks is reflected by less extensive carbonate development, with biotite-amphibole-plagioclase±carbonate proximal to mineralization and biotite-chlorite-hornblende±carbonate developed distally. Mineralization can be vectored using alteration indices that reflect the zonation of K-metasomatism and the carbonate alteration (e.g., increasing ratios of 3K/Al, CO₂/Ca+Mg+Fe; Yeats and Vanderhor, 1998). Other alkalis, including Cs, Rb and Ba, may also be enriched

in areas affected by the mineralizing hydrothermal fluids; the primitive mantle normalized ratio (Cs+Rb)/Th has been suggested as an alteration index (values >5 indicating potentially mineralized sites; Heath and Campbell, 2004).



Figure 9. Typical alteration patterns and element zonation around Archaean greenstone hosted orogenic gold deposits in mafic rocks. A and B are key assemblages in low- and high-grade metamorphic terrains respectively (adapted from Yeats and Vanderhor, 1998).

Other types of hydrothermal ore deposits, particularly cavity fill and breccia-style systems, show more limited or irregular primary dispersion patterns. Mississippi Valley type (MVT) deposits are typically small, discrete, stratabound deposits hosted by permeable zones, faults, karst and hydrothermal cavities in platform or marginal slope carbonate-rich sequences. Host rock alteration around these systems is limited and generally restricted to dolomitization. Some deposits are surrounded by a pyrite-marcasite halo (Dorling *et al.*, 1998). Leakage anomalies and dolomitization (reflected in increased Mg/Ca ratios) may be developed around controlling structures. Hydrocarbons, including C_1 to C_6 alkanes, are commonly associated with MVT and related styles of mineralization and may form extensive haloes around the deposits (Carter and Cazalet, 1984; Wallace *et al.*, 2002; Makhoukhi *et al.*, 2003)

Unconformity-related uranium deposits (e.g., Alligator River province) occur in dilatant structures close to the unconformable boundary between a thick oxidized cover sequence and relatively reduced basement rocks. Mineralization occurs in veins or open, space-filling breccias that extend up into the cover sequence. The unconformity provides a fluid flow path and also represents a chemical contrast between overlying non-reactive host rocks and the chemically reactive basement. The ores were deposited where oxidized fluids carrying U. Au and PGE were reduced and/or underwent an increase in pH. Uranium and Mg are enriched around the mineralization with accompanying Si, Na, Ca and Th depletion. Zones of Cu, Au and As enrichment occur in the upper parts of the deposits, with phosphatic breccias at even higher levels. Anomalous Th concentrations occur in overlying structures, accompanied by elevated REE and Zr contents (Mernagh et al., 1998). Patchy zones of wall rock alteration surround the orebodies and may extend laterally up to 1 km from the site of mineralization (Gustafson and Curtis, 1983; Wilde and Wall, 1987). Alteration is dominated by sericite-chlorite±kaolinite±hematite with Mg metasomatism and strong desilicification at the unconformity. Quartz veining and apatite occur in mineralized structures in the oxidized cover rocks.

In regional metamorphic terrains, it is important to distinguish between mineral assemblages generated by hydrothermal alteration and those formed by metamorphism. These may be very similar for low-grade metamorphism and some types of alteration (*e.g.*, in the outer wall rock zones of porphyry Cu systems or mesothermal deposits, where propylitic alteration assemblages may be nearly identical to those of greenschist facies metamorphism). Careful interpretation of overprinting textures may be required to resolve the issue.

In large hydrothermal systems, additions and depletions of major and minor elements may extend significantly beyond the limit of visible wall-rock alteration and are referred to as 'cryptic' alteration. In some cases, these invisible or low-level effects may be detectable from background host rock variations by geochemical analysis of rock and drill core samples and comparison of element abundances and ratios, covariance or multivariance. For example, Robertson and Taylor (1987) detected depletion haloes around sediment-hosted hydrothermal deposits at Cobar, including extensive depletion of Li (for up to 500 m across strike) and less extensive depletions of Na, K, Sr and Ba (up to 100 m across strike and 250 m along strike). These haloes occur around a number of orebodies at the CSA mine, are coincident with loss of feldspar and sericite from the host metasediments, and are interpreted as depletion during early dewatering processes that preceded mineralization along major structures. Mass balance approaches that use mineralogically constrained modelling of major element whole rock geochemical data are another means of detecting cryptic wallrock alteration. Isocon and Pearce Element Ratio techniques have been successfully applied to detect alteration patterns around the Elura Zn-Pb-Ag deposit near Cobar (Whitbread and Moore, 2004).

DISPERSION ASSOCIATED WITH EXHALATIVE DEPOSITS

Deposits in this major group have formed by hydrothermal fluid exhalation through and onto the sea floor. The fluids can be variably derived from sub-surface magmas or circulated sea or connate waters above zones of high geothermal gradient. The deposits include volcanic associated massive sulphide deposits (VMS) formed in active submarine volcanic settings and exhalative deposits in predominantly sedimentary basins (SEDEX). Both styles of deposit consist of combinations of two types of mineralization: i) a sub-surface feeder system with epigenetic characteristics; and ii) a syngenetic (stratiform or stratabound) mineralization deposited on or just below the sea floor. It is now widely accepted that a major portion of most seafloor deposits formed beneath the surface either by continued fluid infiltration and deposition in earlier formed sulphide mounds or reaction of later fluids with weakly consolidated sulphidic muds. In other cases, sulphide deposition is from pooled metalliferous brines.

The nature of geochemical dispersion reflects the different parts of the deposits. The feeder system generally consists of a cross-cutting stockwork of sulphide-bearing veins and dispersion veinlets with surrounding wall rock alteration and dispersed ore elements (Figure 10). Therefore, minor element dispersion patterns are similar to those associated with epigenetic hydrothermal deposits (*i.e.* of limited



Figure 10. Primary alteration and element zonation around a typical mound style VMS deposit with stockwork-stringer zone and associated alteration pipe (modified after Gemmell et al., 1998).

lateral extent around the vein system but extensive along its vertical dimension). The seafloor component of the mineralization has a mound, lens or sheet-like morphology with extensive lateral element dispersion in the plane of the lens.

In VMS deposits, there is typically upward metal-zoning from Fe to Fe-Cu to Cu-Pb-Zn to Pb-Zn-Ba from the feeder system through to the top of the syngenetic mound or lens (Figure 10). Gold enrichment can occur in the upper parts of these systems, associated with Zn, Ag, Pb and Ba or, in the lower massive and stringer (feeder) zone, associated with Cu (Large 1992). Siliceous exhalites enriched in Fe and Mn commonly extend laterally around the main ore lens. Wall-rock alteration generally consists of an inner zone of silica-pyrite with some chlorite and sericite, a chloritic zone with pyrite and, in some cases, a carbonate and sericite-quartz outer zone. There may be systematic differences in mineral compositions within the footwall feeder system (e.g., white micas are more phengitic in the upflow channels in the centre of the footwall hydrothermal alteration system at the Hellyer deposit, Yang et al., 2004). The general geochemical trend is from Si, Mg, Fe, and Cu enrichment in the centre, with K enrichment and relative depletion in Na and Ca towards the outer part of the system. Alteration may extend into the later deposited hanging wall sequence where hydrothermal activity has continued after burial of the exhalative system. These alteration-related variations in wall-rock geochemistry have been used to locate the inner ore-bearing parts of the systems. For example, K/Na ratios and relative proportions of Rb (which accompanies K) and Sr (which accompanies Ca) have been used in this way. The varying pattern of alteration can be expressed by an alteration index (AI = $100(MgO+K_aO/(Na_aO+CaO+MgO+K_aO))$ and used as a vector to ore where the index trends from 30 to around 100 as the centre of the system is approached (Gemmell et al., 1998).

Stratiform or stratabound components in SEDEX deposits show dispersion of ore elements related to the way that the ore fluids have moved outward from the exhalative vents, either along the sea floor as brines or within sediment layers. These deposits are commonly pyritic and some of the pyrite has probably formed independently by seawater sulphate reduction. As the mineralization is largely syngenetic (formed with, and confined to, a particular sedimentary horizon), dispersion patterns tend to be extensive along strike (up to hundreds of metres or several kilometres) but of limited vertical extent. For example, concentrations of up to 0.5% Zn extend laterally for more than 20 km around the McArthur River Pb-Zn deposit, but only 200 m across strike (Lambert and Scott, 1973). They also have lateral metal zoning (a general pattern of Cu-Fe>Pb>Zn>Mn around the hotter vent, Figure 11). Sequences hosting stratiform Zn-Pb-Ag deposits are anomalous in Zn, Fe, Mn and Tl and other associated elements in the ores include As, Sb, Bi, Cd, Hg and In (Maynard, 1983; McGoldrick and Large, 1998). Many stratiform deposits have extensive Mn haloes (possibly reflecting wide dispersal of Mn in exhaled solution along the sea floor). In a number of Proterozoic deposits, carbonate minerals in the host rocks show increasing Fe and Mn contents towards mineralization. The metal zoning and alteration can provide vectors to ore. For example, the



Figure 11. Some major features and common element zoning of SEDEX deposits (based on Large and McGoldrick, 1998; McGoldrick and Large, 1998).

metal index, Zn+100Pb+100Tl, and alteration index, (FeO+10Mn)100/ FeO+10MnO+MgO, both increase towards ore along strike and, to a lesser extent, across strike (Large and McGoldrick, 1998).

DISPERSION ASSOCIATED WITH MARINE-SEDIMENTARY DEPOSITS

These ores are largely chemical sediments formed from mineral precipitates, generally in extensive, stable marine basins. They include major deposits of Fe (banded iron formations) and sedimentary Mn deposits. Banded iron formations (BIFs) are commonly associated with sequences containing mafic volcanic rocks, shales and dolomites, consistent with a shallow marine shelf depositional environment (e.g., Hamersley Basin, WA). Sedimentary Mn deposits formed in basins commonly related to marine transgressions (e.g., Groote Eylandt, NT). Parts of the modern deep ocean basins contain extensive deposits of Mn nodules, also with associated concentrations of Ni, Cu, Co and Mo (e.g., McKelvey et al., 1979). The source and transport mechanisms for the ore components in these sedimentary deposits of Fe and Mn are unresolved. Possible sources include dissolved and clastic material derived from continental weathering and fluvial run off, wind blown dust, elements dissolved and concentrated from underlying sediments and dissolved material in upwelling ocean currents or in widely dispersed hydrothermal plumes related to submarine exhalative activity (Solomon and Groves, 2000). Some deposits show extensive lateral and limited vertical compositional zoning related to basinal redox conditions and the extent and pattern of element dispersion in solution. These deposits commonly provide the proto-ores for weathering-related supergene or metasomatic enriched deposits of Fe and Mn (e.g., some of the Hamersley Fe deposits and Groote Eylandt Mn ores).

In some BIFs (e.g., Archaean or Algoma type), lateral zoning (over tens of km) is commonly expressed as a facies-type arrangement of oxide-, carbonate- and sulphide-bearing sediments that may reflect changing water depth and redox conditions (Goodwin, 1973; James, 1983). Other deposits are of one predominant facies type (e.g., oxide facies in the Hamersley deposits or carbonate facies in the Middleback Ranges, SA). Micro-, meso- and macro-scale banding is a feature of BIFs. This banding is thought to be related to intermittent or alternating deposition of metal-rich precipitates and silicates. In the Hamersley Group BIF, macro-bands alternate with shale layers and the lower part of the Group (Marra Mamba Formation) shows vertical facies variation, with sulphide-rich assemblages near the base and magnetiterich assemblages in the upper part (Klein and Gole, 1981). Individual macro-bands may show remarkable lateral persistence (>100 km; Ewers and Morris, 1981). The primary geochemical characteristics of BIFs reflect variations in their mineral compositions. Common associated elements include Mg, Al and Ti in Fe silicates, Mn, Mg and Ca in Fe carbonates, S and As in sulphides and P in apatite. During weathering and leaching, these elements are commonly released and variably incorporated into secondary Fe oxides (e.g., Al and P in goethite). The BIFs of different ages show some differences in their trace element contents but are generally enriched in Mn, Co, Sc, Y and Eu relative to average crust (Maynard, 1983).

The geochemical behaviour of Mn is similar to that of Fe, being strongly controlled by redox changes. However, Mn is stable in solution over a wider Eh-pH range, particularly under moderately reducing conditions. Sedimentary Mn ores appear to form where special chemical conditions cause separation of Mn from Fe, and precipitation of Mn as hydroxides, oxides and carbonates. For example, a limited increase in pH may lead to the selective elimination of Fe from Fe-Mn bearing solutions, and a further increase in pH or Eh can then cause formation of stable Mn oxides or carbonates (Maynard, 1983). Basin-scale lateral facies variations have been described and explained by variations in redox conditions with water depth (e.g., for the giant Nikopol deposit in Ukraine). These include an oxide facies, a mixed oxide-carbonate facies and a carbonate facies with increasing depth, although it is unclear whether part of this variation may be due to supergene processes (Varentsov and Rakhmanov, 1977). At Groote Elyandt, pisolitic and disseminated Mn mineralization occurs in two main basins. In the northern basin, the primary Mn oxide ore consists of ooliths and pisoliths, subsequently cemented and modified by diagenetic, supergene and pedogenic processes into concretionary and massive material forming a layer up to 9 m thick, extending over an area of 22 x 6 km (Bolton *et al.*, 1990). In the SW basin, carbonate-bearing manganiferous rocks may represent a deeper water facies flanked by disseminated Mn oxides. Associated elements in these ores include Al, Ba, Ca, Fe, K, Li, Mg, P and Zn. Their relative abundance and distributions are largely controlled by the dominant Mn minerals (reflecting depositional conditions and later alteration), and by the presence of Fe oxides and detrital components (Ostwald, 1988). Manganese oxides have a high capacity to take up cations such as Co, Ni, Cu and Pb and may be enriched in these elements where they have been available for adsorption or substitution.

DISPERSION RELATED TO METAMORPHIC PROCESSES

Many ore deposits have resided in the crust for long periods under both prograde and retrograde metamorphic conditions. Primary dispersion patterns around ore deposits are commonly preserved during prograde metamorphism, particularly if there is limited fluid movement. New metamorphic minerals formed in the orebody or wall rocks may 'lock in' elements originally dispersed during ore formation. For example, metamorphosed exhalative deposits commonly have Mn-rich garnets in the footwall rocks (e.g., Broken Hill). Gahnite (Zn-bearing spinel) and Pb-bearing feldspars also occur in the lode horizon rocks at Broken Hill. Metamorphosed massive sulphide deposits may show sulphidation and oxidation haloes (extending up to at least 40 m) where sulphur and oxygen components from the sulphide deposit have reacted with the Fe component of ferromagnesian silicates to produce more Mg- or Zn-rich silicates or Zn-rich oxides (Spry, 2000). The extent of these haloes is a function of the gradient in O or S fugacity around the deposit during metamorphism and is controlled by the ore and host rock composition, particularly the abundance and proximity of reduced carbon or graphite in surrounding metasedimentary rocks. Zinc staurolite (with a distinctive orange brown colour) occurs in and around metamorphosed sphalerite-bearing ores and has been suggested as a useful indicator of proximity to metamorphosed sulphide deposits (Spry and Scott, 1986).

Ore deposits formed from submarine exhalations are commonly surrounded by laterally more extensive non-ore exhalites. During regional metamorphism, these form meta-exhalites with distinctive mineralogies including magnetite-, silicate- and phosphate-bearing iron formations, garnet-quartz rock, quartz-gahnite rock, barite-rich rocks and tourmalinites (Spry et al., 2000). Mineralogical and bulk geochemical variation in these meta-exhalites commonly relate to primary zoning in the exhalite and may be useful in exploration to vector towards ore. Minerals and element ratios that reflect the increasing contribution of the exhalative component relative to detrital material as ore is approached appear to be the most useful vectors. Typically Fe, Mn, B, P and Zn indicate a hydrothermal-exhalative source and Al and Ti a clastic source. Thus, Fe+Mn/Al, Fe/Ti, Mn/Ti and P/Ti ratios and increasing concentrations of ore and associated elements (e.g., Cu, Pb, Zn, Ag, As, Au, Bi, Cd, Co, Hg, Mo, Ni, Sb, S, Se, Te, Tl, F and Cl) are suggested as useful geochemical indicators to ore proximity (Spry et al., 2000).

Metamorphosed hydrothermal alteration zones show metamorphic mineral assemblages that reflect the elemental composition of the original alteration pattern. For example, where there has been mediumto high-grade metamorphism, zones of sericitic alteration may be preserved as mica schists, and chloritic alteration by cordierite- and anthophyllite-bearing assemblages.

Deformation, with or without accompanying regional metamorphism, can significantly change the geometry of ore systems and result in displacement, flattening or folding of associated alteration zones and primary dispersion patterns. Some of the ore components, particularly massive sulphides, may be mechanically remobilized. Thermal recrystallization can result in textural changes to the ores, particularly grain coarsening, which may have positive benefits for processing and beneficiation.

Hydrous metamorphism and associated deformation may lead to remobilization of elements and the formation of leakage haloes along structures. This is particularly likely during near-surface retrograde metamorphism involving circulating meteoric fluids or where later fluid-rich melts have been intruded into the crust. Such leakage haloes represent an additional geochemical expression that may extend considerable distances from major ore deposits and could be used in exploration for blind deposits. For example, retrograde schist zones at Broken Hill have been suggested as suitable structures in which to search for potential leakage anomalies from buried mineralisation (McQueen, 1995). Similarly, Williams and Smith (2003) have documented Pb-Zn enrichments in amphibolites near the Cannington and Maramungee 'Broken Hill-type' deposits in the Mount Isa Inlier. These dispersions formed during retrograde metamorphism of the deposits and extend up to at least 140 m from significant Pb-Zn-Ag sulphide zones.

DISPERSION ASSOCIATED WITH RESIDUAL AND SUPERGENE DEPOSITS

Elements that are released, complexed and dissolved under nearsurface weathering conditions may be leached and redistributed in the weathering profile or concentrated by groundwaters to precipitate elsewhere. Other elements, hosted by stable primary or secondary minerals may be concentrated by residual enrichment. Lithology, structure, geomorphology, climate and climatic history, hydrological factors, redox boundaries and varying pH within the chemical weathering profile control patterns of primary and secondary dispersion in these deposits. Well-known examples (under oxidizing conditions) include concentrations of Fe and Mn oxides/oxyhydroxides, and Al oxides/ oxyhydroxides. Elements such as U and V are mobilized under acid, oxidizing conditions and can be leached from source rocks, transported in groundwater and selectively redeposited (e.g., as calcrete and organic-associated U deposits in palaeochannels, in oxidizing and reducing environments, respectively). Gold and Cu are mobilized under appropriate weathering conditions and can be redistributed to form supergene deposits within the residual regolith or in adjacent or overlying sedimentary units. Bauxites, Ni-Co laterites, some Fe and Mn ores, and phosphate (Nb-REE) deposits on carbonatites are largely the result of residual enrichment; the characteristics of these deposits and supergene Au mineralization, are reviewed by Freyssinet et al. (in press).

Lateritic bauxites (Figure 12) are a major deposit type in Australia. These have formed by chemical leaching of weathering profiles developed on a variety of parent materials including granitic and gneissic rocks, clay- and feldspar-rich sediments and basalts. Weathering of



Figure 12. The components and mineralogy of a generalized section through a bauxite deposit (after Anand and Butt, 2003). Element abundance trends are for the Weipa bauxite (Evans, 1965).

feldspars and clays under humid, alkaline to mildly acid conditions results in removal of K, Na, Ca and Mg, with residual enrichment in Al and Fe. Many of the resultant bauxites have formed essentially in situ (e.g., Darling Range deposits, WA) but the degree to which others (e.g., Weipa) have been mechanically transported and enriched is not resolved. The bauxite is developed above the mottled zone (Figure 12) and deposits are typically 1-5 m thick. Most deposits have associated Fe-rich layers and overlie kaolinitic saprolite. In some deposits (e.g., Darling Range), ferruginous duricrust and gravels overlie the bauxite (see Figure 12). The deposits are commonly pisolitic or nodular and consist mostly of gibbsite with minor boehmite. They typically show vertical mineralogical and chemical zoning marked by increasing gibbsite and decreasing boehmite abundance with depth, reflecting increasing activity of water. Iron and Si are depleted in the gibbsiterich zone and increase below this. Titanium (mostly as anatase) shows relative enrichment up the profile (Evans, 1965; Somm, 1975; Joklik et al., 1975).



Figure 13. Major features and element dispersion characteristics of the main types of supergene Au deposit (adapted from Butt, 1998). A. Residual (lateritic) deposit formed during humid climate. B. Saprolitic deposit formed during arid climate. Remobilised Au precipitates at water table levels and/or lower redox fronts within the saturated zone.

Gold may concentrate residually as a stable mineral or be mobilized as halide, thiosulphate or organic complexes. Secondary Au deposits form during intense chemical weathering of primary Au mineralization and can be subdivided into lateritic and saprolitic types, depending on their position within the weathering profile (Butt, 1998). Lateritic deposits (Figure 13A) occur as flat lying zones (2-10 m thick) of Au enrichment in the upper part of the profile within the ferruginous and mottled zones of lateritic profiles. They contain both residual primary and secondary Au and, in the Western Australian examples, they have extensive multi-element haloes of Au±Ag, As, Sb, Bi and W, reflecting residual element associations from the primary mineralization. Under arid conditions, where groundwaters are saline, mobilized Au precipitates deeper in the profile, close to the water-table or at related redox fronts. This can result in one or more near horizontal zones of Au enrichment in the saprolite (Figure 13B) particularly if there have been several still-stands in the water-table. In these saprolitic, supergene deposits, most of the Au is secondary and of high fineness, but residual primary Au increases towards the base. There is no enrichment in associated pathfinder elements, although higher Mn and Fe concentrations may mark the redox boundary (Butt, 1998). Commonly, there is a Au depletion zone 5-25 m thick between the upper laterite hosted (residual) mineralization and the underlying saprolitic supergene zone. Other primary pathfinder elements such as As, Sb, Bi, K, Pb, Rb and W may be preserved in this zone. The shape of saprolitic deposits can vary, depending on the width of the primary mineralization and groundwater conditions. They are typically mushroom- or nailshaped (e.g., at a grade concentration of 1 g/t), but overall rarely extend laterally more than a few metres beyond the weathered primary mineralization as defined by its alteration halo. Many, mostly small,

Au deposits in Western Australia are associated with palaeochannels, as sub-horizontal enrichments within the sediments or the saprolite beneath the channel. Most are oxidized, but some enrichment occurs in lignite. Although a detrital, placer origin is possible for those in sediments, the Au is generally secondary and they are probably a type of chemically-deposiedt supergene mineralization. Gold dispersion during weathering and the formation of secondary Au deposits are discussed further in the chapter on Geochemical dispersion, process and exploration models (*this volume*).

Nickel laterites form by residual enrichment of Ni, Co, Fe and Mn over chemically weathered ultramafic rocks. Leaching of Mg±Si causes Ni and Fe to become relatively enriched in the upper part of the profile in oxide-rich material. Nickel released by recrystallization and dehydration of Fe oxyhydroxides is leached laterally and downwards, either to form hydrous Ni-rich silicates, by exchange with Mg in serpentine or by reprecipitation with Si and Mg in a variety of mostly poorly-crystalline phases ("garnierite"), or to form Ni-bearing smectites in the saprolite. The major controls on this process are climatic, geomorphological, hydrological, lithological and structural. Hydrous silicate Ni enrichment occurs in strongly leached, freely drained environments, whereas smectitic deposits occur in less leached or less well drained settings (Brand et al., 1998). Residual Ni is concentrated with Co and Mn within the upper ferruginous part of the regolith in goethite and Mn oxides. The primary geochemical expression is marked in the near surface by increased Fe (>40%), Si/Mg (>200) and Ni/Cu (>40) and widespread Ni±Co-Mn anomalies along strike and over the host ultramafic body (Brand et al., 1998). Other associated trace elements include Cr and Zn. Nickel mobility during weathering and the formation of Ni laterites are discussed further in the chapter on Geochemical dispersion, process and exploration models (this volume).

DISPERSION AROUND PLACER DEPOSITS

The primary geochemical expressions of placer deposits reflect the varying heavy mineral composition of the deposits and the degree of concentration and sorting of the detrital minerals. Concentration is largely controlled by hydraulic equivalence, if grains are being transported by saltation or suspension, and entrainment equivalence and interstice entrapment under conditions of traction transport (Evans, 1993). Dispersion patterns relate to the sedimentological controls on



Figure 14. Common placer gold occurrences and the concentration patterns found in fluvial systems (based on Boyle, 1979; Best and Brayshaw, 1985; Swensson, 1990). A. Section of confined valley-fill (lead) system. B. Plan showing typical sites of concentration in moderate gradient rivers.

deposition and reworking. The associated heavy mineral suite (*e.g.*, magnetite-ilmenite black sands with Au; kimberlitic indicator minerals with diamond) can provide a more extensive expression to the placer concentration. Mineral inclusions in the heavy minerals (*e.g.*, sulphides in cassiterite) may provide an additional geochemical signal. These associated elements in placers can give rise to post-depositional dispersion anomalies detectable during exploration. For example, Sn placers in fluvial channels buried by marine sediments on the Siberian Arctic shelf have associated linear anomalies of Ag, Mo and Zn (Patyk-Kara, 1999).

Most Au placers have formed in alluvial systems (although there are examples of eluvial, colluvial and beach deposits) and their geometry reflects channel morphology and particular energy regimes in the channel system. Many have undergone multiple stages of reworking and increased concentration. Early Tertiary deep leads in Victoria (Figure 14A) consist of upward-fining sequences with coarse gravel 'wash' at the base overlain by a dominant sandy 'drift' and a thinner upper clay-rich layer. Gold is concentrated in the basal gravels, at or close to the underlying weathered basement (Swensson, 1990). The Au composition in placers largely reflects the composition of the primary Au with some changes due to physical and chemical processes during and after weathering, transport and deposition (e.g., Knight et al., 1999; Chapman et al., 2000). In some cases, the trace element characteristics of the Au can be used to trace the source. In the Victorian deep leads, such geochemical trains extend for 1-5 km from the primary source (Swensson, 1990). Alluvial Au can show high fineness (low-Ag) rims or coatings and evidence of chemical corrosion, suggesting chemical mobilization of Au. This is particularly likely where chloride or organocomplexing of Au has been possible and raises the possibility of Au dispersion patterns related to hydrological and chemical controls in alluvial placer systems. In comparison, as noted above, many small deposits in (and beneath) palaeochannels in Western Australia consist dominantly of secondary Au and appear to be chemically-precipitated supergene deposits (chemical placers).

Heavy mineral sand deposits (Figure 15) are generally associated with fossil beach strandlines and appear to have formed by cycles of marine transgression and regression (*e.g.*, Baxter, 1990). Variations in placer composition are largely due to differences in heavy mineral abundances in the sediment provenance coupled with some separation of different heavy minerals by varying energy regimes. At Eneabba, in Western Australia, grading by wave action under high energy regimes has



Figure 15. Examples of heavy mineral sand deposits showing the main features and concentration processes. A. Simplified section of part of the Eneabba deposit, WA (after Lissiman and Oxenford, 1975). B. More detailed section based on the Yoganup deposit, WA (after Welch et al., 1975).

TABLE 2 PRIMARY GEOCHEMICAL DISPERSION AROUND MAJOR ORE DEPOSIT TYPES

Magmatic deposits

- Gradational ore element concentrations above or peripheral to ore, reflecting incomplete ore mineral segregation.
- Geochemical evidence of ore-forming processes (magma contamination/mixing, S saturation, ore element depletion in host body).

Skarn deposits

- Distinctive mineral zoning related to thermal and chemical gradient from intrusion to reactive country rock.
- Ore element patterns also related to prograde vs retrograde evolution of system.

Hydrothermal stockwork/porphyry associated deposits

- Broad, diffuse pattern of element dispersion with metal zoning.
- Widespread and distinctive, zoned wall rock alteration.

Hydrothermal vein deposits

- Intense, narrow pattern of ore element dispersion around veins, depending on host rock permeability and chemistry. Wall rock alteration may be distinctive.
- Dispersion more extensive along vein system with possible element zoning related to varied conditions along fluid path.

Hydrothermal replacement deposits

- Dispersion controlled by degree of disequilibrium between fluids and host rocks and level of diffusion/interaction. Metal zoning/overprinting in multistage systems.
- Alteration effects (silicification, chloritization, sericitization carbonate alteration) may be extensive.

Exhalative-diagenetic deposits

- Stratiform/stratabound components show laterally extensive and zoned element dispersion along strike.
- Feeder systems show vertically extensive dispersion and distinctive, zoned wall rock alteration.

Marine sedimentary deposits

- Extensive lateral and limited vertical compositional zoning related to depositional conditions.
- Trace element characteristics reflect major mineral (oxide, silicate, carbonate, sulphide) assemblages.

Metamorphosed deposits

- Pre-metamorphic dispersion and alteration patterns may be preserved in metamorphic assemblages.
- Sulphidation/oxidation haloes in enclosing silicates or leakage haloes related to hydrous metamorphism.

Residual and supergene deposits

- Element dispersion controlled by climate, geomorphology, hydrologic factors, redox boundaries and varying pH in weathering profile.
- Commonly show vertical mineralogical/chemical zoning with variable preservation of primary trace elements associations.

Placer deposits

- Element dispersion patterns related to sedimentalogical controls on heavy mineral deposition and reworking.
- Associated non-ore heavy minerals and mineral inclusions may provide a geochemical signature.

concentrated heavier zircon and monazite relative to rutile and ilmenite at particular locations (Shepherd, 1990). Monazite-bearing deposits may contain sufficient thorium to be detectable by radiometric methods.

SUMMARY

Primary ore deposit expressions, particularly ore-host rock relationships and element and mineral distributions, are key guides for mineral exploration in unweathered rocks and for deep or blind ore systems. They can be more important than the prevailing theories of ore genesis, even though genetic models may help explain the expressions. Knowledge of primary dispersion and associated alteration can also assist in interpreting secondary element dispersion patterns and ore deposit expressions in the weathering of primary patterns or leakage anomalies, as well as from the orebody itself. Identifying the secondary signal of primary dispersion, as distinct from secondary dispersion from the ore, can help in drill targeting. Appropriate interpretation of geochemical data from weathered host rocks can also identify the primary wall rock alteration, where there is some knowledge of the likely primary minerals.

The key primary geochemical dispersion characteristics of the major ore types are summarized in Table 2.

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