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Tectonic controls on gold deposits and their environmental impact, New Zealand

D. Craw*

Department of Geology, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Abstract

New Zealand is an active orogenic belt which varies along its length from continental collision to continent–ocean subduction tectonics. Mesothermal gold deposits, with rare mercury, have formed in collisional settings from late Mesozoic to Pleistocene, with youngest deposits along the axis of the actively rising Southern Alps mountain chain. Epithermal gold and mercury deposits have formed, and are still forming associated with calcalkaline volcanism above the subduction zone, and with basaltic volcanism associated with extensional faulting. The environmental impact of mineral deposits is related to tectonic setting, mineralogy, and climate, all of which are governed by the geometry of the orogen. Mesothermal mineralisation added carbonates to calcite-bearing host rocks in what is now cool semiarid or extreme Alpine settings, and oxidation of sulphides does not result in significant acidification of the environment. Arsenic is the principal metal of environmental significance, and is readily mobilised from these deposits at neutral to alkaline pH. Mercury may be leached from cinnabar and/or gold on geological time scales. In contrast, epithermal mineral deposits have hydrothermal clay alteration, locally further clay-altered by deep temperate to subtropical weathering, and calcite is generally subordinate to sulphides. Acidification accompanies oxidation of these deposits, and copper, cadmium, lead and zinc are readily mobilised into the environment. Mercury can be mobilised by these acid solutions as well, where mercury occurs in minerals other than cinnabar. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: acid mine drainage; climate; collisional tectonics; mesothermal; epithermal

1. Introduction

The islands of New Zealand are an active orogenic belt in the South Pacific Ocean. The islands owe their emergence above sea level to this active orogenesis. The nature of the orogenic processes varies along the length of the orogen, and consequently the topography and topography-affected climate vary along the orogen. Mineral deposits, particularly gold, have formed, and are still forming, along the orogen and the nature of these deposits varies according to position in the orogen as well. Basement rocks are essentially uniform for the mineralised portions of the orogen, over a distance of nearly 1500 km. Deposit mineralogy is therefore related to specific tectonic setting. The environmental impacts of mineral deposits, as natural exposures and as a result of mining, are governed by deposit mineralogy, topography and climate. Since all these factors are affected by tectonic setting in the New Zealand orogen, environmental impacts can be broadly related to tectonic setting.

This paper summarises the variations in geological

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* Fax: +64-3-479-7527.
E-mail address: dave.craw@stonebow.otago.ac.nz (D. Craw).

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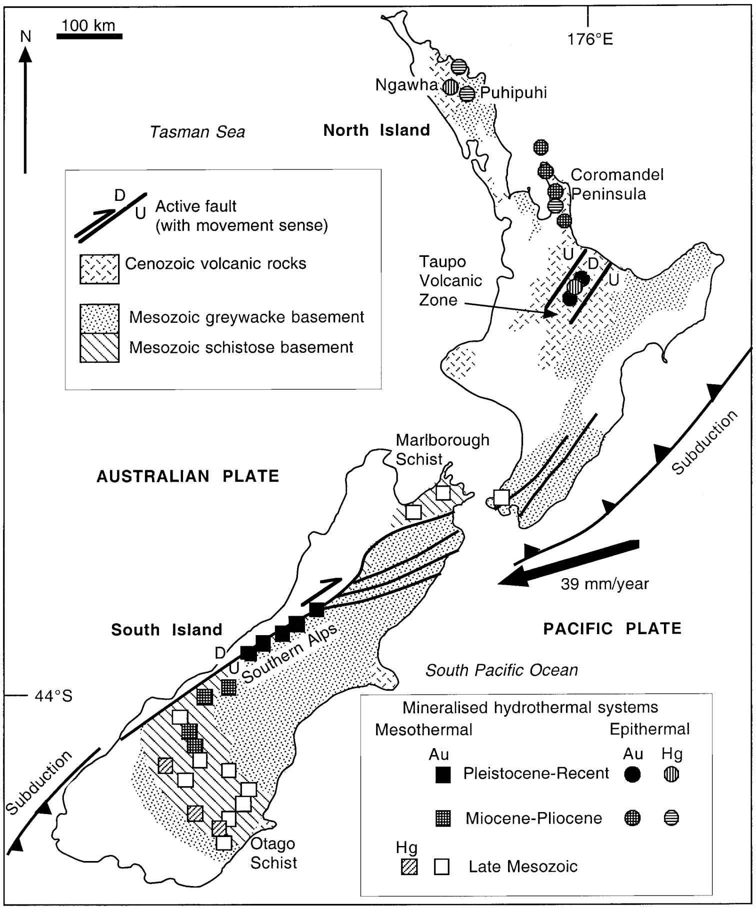

Fig. 1. Generalised geological map of the Pacific-Australian plate boundary through New Zealand, with a current plate vector (after Walcott, 1978; ; DeMets et al., 1990) and main active faults (D = downthrown; U = upthrown). Principal mineral deposits of both epithermal and mesothermal style (after Williams, 1974; Brathwaite et al., 1989; Craw and Norris, 1991; Cox et al., 1997) are shown in their tectonic context.

and mineralogical style of orogenic mineral deposits along the New Zealand orogen and relates these variations to tectonic setting. Then the environmental impacts of different deposit types are examined in the context of their mineralogy, topographic setting and climate, to provide a regionally predictive framework for expected acid generation and metal mobility along the orogen. This framework can be used as a background for environmental management of mineral deposit exploitation.

2. Tectonic setting

New Zealand consists of two main islands, North and South Islands (Fig. 1), with basement rocks consisting of a range of terranes accreted in the Mesozoic. The dominant basement rocks are Mesozoic metagreywackes and their schistose equivalents (Fig. 1), and these are the rocks of principal interest in this study. The islands lie on and adjacent to the Australia–Pacific plate boundary which has resulted in late Cenozoic modification of the basement rocks in the exposed landmass. The plate boundary in the South Island is an oblique strike-slip fault, the Alpine Fault (Fig. 1), which has offset basement terranes by nearly 500 km dextrally. This portion of the plate boundary has been undergoing continent–continent collision since the late Miocene, resulting in uplift of metagreywacke basement to form the Southern

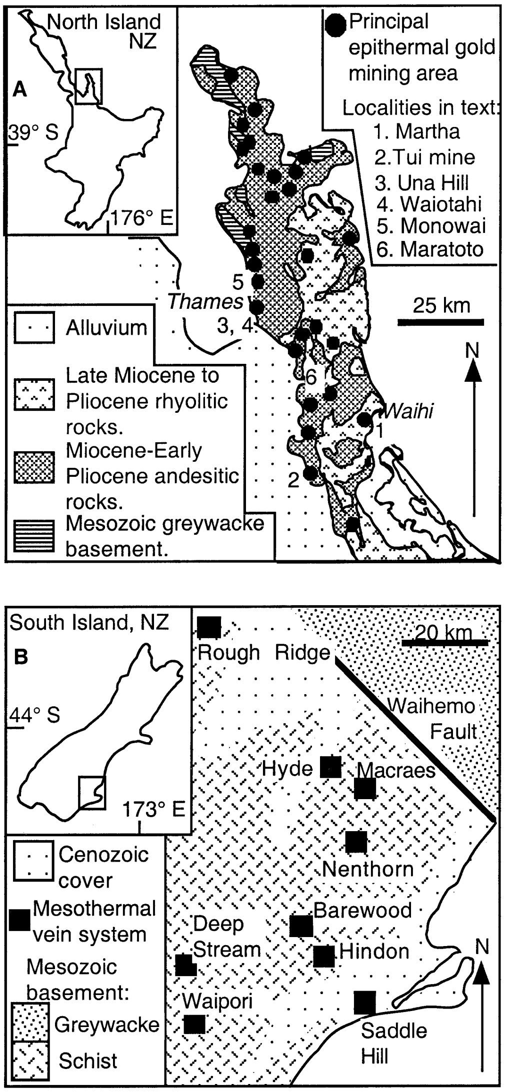

Fig. 2. Regional geological maps of the epithermally mineralised Coromandel Peninsula (A) and mesothermally mineralised east Otago (B) areas, with their principal mineral deposits including those mentioned in the text. Localities are from Williams (1974).

Alps mountain chain (Fig. 1). The plate boundary at the southern end of the Alpine Fault is a subduction zone which dips steeply east beneath the South Island and continues into the Southern Ocean (Fig. 1; Walcott, 1978).

The northern end of the Alpine Fault has evolved into a dominantly strike slip fault system in the northern South Island and southern North Island (Fig. 1), with associated uplift of metagreywacke mountain ranges. The plate boundary continues offshore and merges with a west-dipping subduction zone to the east of the North Island (Fig. 1; Walcott, 1978). This subduction zone dips beneath the metagreywacke basement of the North Island, where crustal extension is occurring above the subduction zone. Calcalkaline arc magmatism has resulted in active volcanoes and associated deposits overlying the basement in the central North Island (Fig. 1; Cole, 1979). Extensional faulting in the north of the North Island has localised mantle-sourced alkaline to tholeiitic basaltic magmas; these are not currently active (Hodder, 1984; Smith et al., 1993).

The plate boundary geometry has been evolving since the Oligocene (Carter and Norris, 1976), but the principal features of the present plate boundary have been in place since the Miocene. In particular, the Southern Alps have been rising in the south since the early Miocene (Craw, 1995), and there has been calcalkaline magmatism in the North Island since the early Miocene (Cole, 1979) (Fig. 2A). Basaltic volcanism in the far north of the North Island was initiated in the Pliocene and persisted to the Recent (Smith et al., 1993).

3. Mesothermal mineralisation

Gold mineralisation was widespread in Mesozoic metagreywackes of the South Island (Fig. 1). Deposits have a mesothermal style (Nesbitt, 1991) and most are hosted by the Mesozoic Otago Schist and its faulted extension, the Marlborough Schist (Fig. 1). The term ‘mesothermal’ as used here refers to a set of vein-hosted deposits formed at a variety of depths and temperatures in continental collisional tectonic setting. The most gold-rich and therefore most exploited portions of the mesothermal mineralising systems were formed in the middle crust. Shallower portions of these hydrothermal systems are included in the term ‘mesothermal’ because they are genetically related. As such, these vein systems are distinct from the ‘epithermal’ systems described below from different tectonic settings in the same New Zealand orogen.

Gold occurs in quartz veins which cut the schist at a variety of angles as they fill fault zones which range

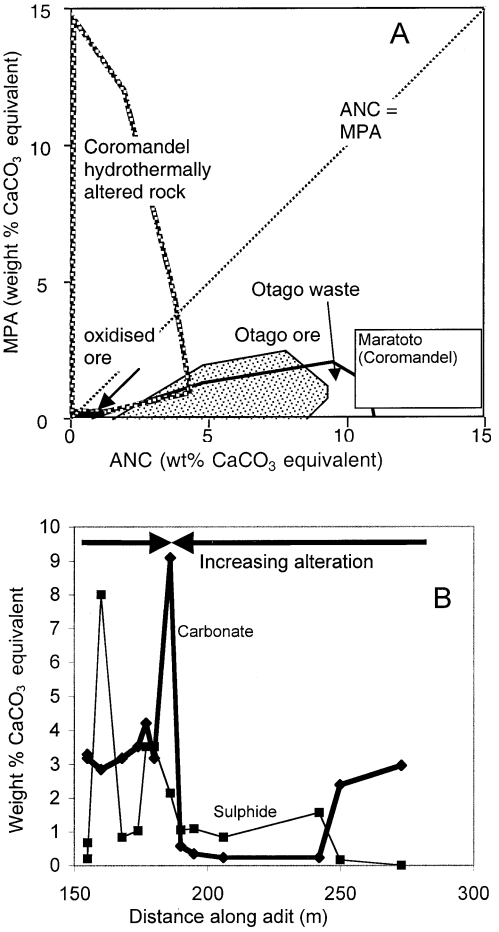

Fig. 3. Comparison of acid neutralising capacity (ANC) and maximum potential acidity (MPA) in mesothermal (Otago) and epithermal (Coromandel) mineral deposits. (A) Mineralised (stippled) and unmineralised rocks (no ornament) from Otago, principally from the vicinity of the Macraes mine (Fig. 2B), lie below the ANC = MPA line. Hydrothermally altered and mineralised rocks from the Coromandel area (principally near Waihi, Fig. 2A) lie mainly above the ANC = MPA line except for the Maratoto mine (Fig. 2A; see text). (B) Comparison of ANC and MPA, calculated from CO_2 and S contents, respectively (from Weissberg and Wodzicki, 1970), with distance across a base metal rich epithermal mineralised zone, Tui mine (Fig. 2A).

from 30 cm to 100 m in width (Williams, 1974; Craw and Norris, 1991; Brathwaite and Pirajno, 1993). The veins contain minor amounts (upto 2%) of sulphides: dominantly pyrite and arsenopyrite, with traces of chalcopyrite, sphalerite and galena. Arsenic has been added to the rocks during mineralisation, but base metals have not and the base metal sulphides are due to sulphidation of background trace metal contents (Fig. 3A and B). Calcite occurs as an important vein mineral, and as thin veinlets in host schist. Alteration of the host schist is minor, and generally extends for only centimetres or metres from a quartz vein (Williams, 1974; McKeag et al., 1989). Alteration consists of silicification and addition of carbonate (calcite, ankerite and/or siderite) and scattered sulphides along vein margins. Beyond the narrow alteration zone, the schist remains unaffected by hydrothermal activity and has simple mineralogy: quartz, albite, muscovite, chlorite, epidote, calcite and titanite with rare iron sulphides or oxides. Similar but minor mineralisation occurred in metagreywacke in the southern North Island (Fig. 1; Williams, 1974; Brathwaite and Pirajno, 1993).

Most mineralisation occurred during late Mesozoic uplift of the schist belts, including the only actively mined deposit, at Macraes (Fig. 2B). Mineralisation occurred at a variety of crustal levels during this uplift, from near the brittle–ductile transition to the upper 2 km of the crust (Craw and Norris, 1991). Shallow-formed deposits have stibnite as a minor accompanying mineral, and deeper formed deposits have scheelite which has been mined historically. Cinnabar–pyrite occurrences (Fig. 1) attest to relict shallow-level mineralisation. Gold contents of known cinnabar deposits are low, but some rich alluvial gold deposits have been derived from cinnabar-bearing vein systems (Youngson et al., 2001).

Gold deposits formed during the inception of the Alpine Fault in the Miocene (Cooper et al., 1987; Craw, 1989), and some of these deposits have been mined historically. The deposits formed in Otago Schist at the southern end of the Southern Alps (Fig. 1). Miocene deposits structurally, texturally and mineralogically resemble the shallower-formed late Mesozoic veins, and consist of well-defined quartz veins with host rock alteration on a scale of millimetres to centimetres only. Ankeritic carbonate is common but is always accompanied by calcite. Stibnite-bearing veins with low gold contents occur in close association with these Miocene gold-bearing veins.

Further gold deposits formed, and are forming, near the crest of the Southern Alps in the principal zone of collisional uplift (Fig. 1). These deposits have formed at a wide range of depths from near-surface (<1 km) to several kilometres (Cox et al., 1997). The deposits are small and few have been mined in situ, but gold eroded from this deposit type has accumulated on beaches of the west coast of the South Island (Fig. 1) and has been mined sporadically for 150 years (Craw et al., 1999). The primary veins are narrow (cm–m scale) and fill localised extensional fractures or brecciated fault zones. Many veins are quartz-free and dominated by ankerite and calcite with minor suphides (pyrite, arsenopyrite) which pervade host rock and breccia fragments. Some veins have quartz with ankerite, calcite, pyrite and arsenopyrite and resemble the Miocene veins formed farther south (above). Late stage calcite veins fill many faults and fractures throughout the mountains, and many of these veins have elevated arsenic levels (Horton et al., 2001) indicative of mesothermal vein style, although gold is not always present.

4. Epithermal mineralisation

4.1. Exploited gold deposits

Mineral deposits in the North Island generally have an epithermal style and are associated with late Tertiary to Recent igneous activity described above (Fig. 1). Deposits which have been mined historically and currently are located in or near the Coromandel Peninsula (Figs. 1 and 2A; Brathwaite and Pirajno, 1993). The basement rock is Mesozoic metagreywacke, but this is only locally exposed due to extensive cover of late Tertiary volcanic rocks (Fig. 2A). The volcanic rocks exhibit a wide range of compositions, but they are dominantly andesitic in the west and rhyolitic in the east. Gold-bearing vein systems cut all rock types including basement greywacke, and are strongly structurally controlled, mainly by normal faults (Weissberg and Wodzicki, 1970; Merchant, 1986). Quartz veins range from 30 cm to 10 m in width, and commonly occur in sub-parallel swarms. Most veins formed within 2 km of the surface, although some deeper systems, which have similarities to porphyry copper deposits, occur also (Merchant, 1986).

In addition to the quartz veins, the mineralisation systems are characterised by widespread hydrothermal alteration of the host rocks. This alteration is zoned, with intensity of alteration increasing towards the main vein systems over hundreds or even thousands of metres. The least altered rocks have undergone propylitic alteration which resulted in albitisation and sericitisation of feldspars, chloritisation of mafic minerals, and addition of calcite and pyrite. Propylitic alteration occurs over hundreds of square kilometres of the Coromandel Peninsula (Skinner, 1993). More intense alteration nearer veins (within 100 m) results in an argillic zone which is characterised by alteration of most minerals to clays and sericite, and addition of pyrite (upto 10% locally).

The most intense alteration, of quartz–sericite type, occurs within metres or tens of metres of the veins. This zone is characterised by sericitic alteration and extensive silicification, with widespread introduction of pyrite. Calcite is rare in the argillic and quartz–sericite zones, but occurs locally as an important component of the main veins. Pyrite is commonly accompanied by other sulphides such as chalcopyrite, sphalerite and galena, and a wide variety of accessory metallic minerals including antimony sulphides and gold (Williams, 1974; Merchant, 1986; Brathwaite and Pirajno, 1993). These additional sulphides are most common in the major quartz veins and associated quartz–sericite zone. Base metals have been added to the rocks, resulting in substantial metallic enrichment locally.

4.2. Active geothermal systems

Recent and active geothermal systems occur to the northeast of the active calcalkaline volcanoes of the Taupo Volcanic Zone (Fig. 1). Volcanism and associated geothermal activity are structurally controlled on a regional scale by normal faults of the extensional region above the subduction zone (Cole, 1979; Fig. 1). Many of the active geothermal spring sytems have evidence for metallic mineralisation, including gold, arsenic, and mercury, and metal contents of discharge waters are high (Weissberg et al., 1979; Brathwaite and Pirajno, 1993). Widespread alteration of host rocks has occurred around most geothermal systems (Browne, 1978), similar to that described above for the Coromandel epithermal veins.

Active hot springs at Ngawha in the far north of the North Island (Fig. 1) are related to young basaltic volcanism in the area. These springs have high mercury contents, resulting in elevated Hg contents of nearby streams, and deposits of cinnabar and liquid mercury near spring discharge points (Davey and van Moort, 1986).

4.3. Mercury deposits

There are several epithermal mercury deposits in the North Island in addition to the elevated levels of mercury in active geothermal systems described above (Fig. 1). These deposits are associated with epithermal gold bearing systems in the calcalkaline setting of the Coromandel area and the extension-related basaltic magmatism of the Puhipuhi area (Fig. 1). The Puhipuhi area has the best developed deposits, which have been mined historically for mercury (Henderson, 1944; White, 1986) and prospected more recently for gold. The basement in the area is metagreywacke overlain by Pliocene lake sediments and basalts. Hydrothermal activity at Puhipuhi was controlled by north striking faults, and rocks adjacent to these structures have been variably silicified and/or altered to clay mineral assemblages on the 10 m scale. Hydrothermal mineralisation resulted in deposition of cinnabar, stibnite, pyrite, and marcasite, with minor gold and silver.

5. Environmental impacts

The environmental impacts of the mineral deposits formed, and forming, along the plate boundary through New Zealand are a direct result of interactions between the mineral assemblages of the deposits, the way the minerals respond to oxidation in the prevailing climate, and the nature of the host rocks. The environmental impacts of the deposits vary along the plate boundary according to the tectonic setting, which controls deposit mineralogy, and also controls the climate which is affected by tectonically induced topography. The principal differences in environmental impact arise between the mesothermal deposits of the South Island and the epithermal deposits of the North Island (Fig. 1). These differences are investigated below in the context of acid rock drainage and metal mobility. Acid rock drainage is best examined in terms of maximum potential acidity and acid neutralisation capacity of rocks, and the balance between these parameters.

5.1. Climate and weathering

Climate varies along the plate boundary, and New Zealand can be subdivided into three principal climatic zones in which mineral deposits occur. The mesothermal deposits of Otago and Marlborough lie in a pronounced rain shadow, which has developed as the Southern Alps have risen since the Miocene to form a barrier across the generally westerly winds of the South Pacific Ocean (Chamberlain et al., 1999). Most of this region is cool and semiarid, with rainfall less than 700 mm/year. Vegetation is mainly grasses and shrubs, and trees are sparse. Evaporation rates can exceed precipitation rates, and soils commonly contain evaporative calcite deposits, with soil pH from 7 to 8.5. Soils are highly lithic and thin (commonly <1 m), and oxidation of fresh rock rarely extends below 3 m. Extensive kaolinitisation of the bedrock surface occurred in the Tertiary, but most of this veneer has been stripped during late Cenozoic uplift and erosion. Oxidation associated with this kaolinitisation extends to less than 10 m on hillsides and hill crests.

Mesothermal deposits along the crest of the Southern Alps occur in an extreme Alpine climatic zone. Precipitation ranges from 2000 to >5000 mm/year, and the deposits are buried under snow for several months at a time. There is little or no soil, fresh rock is exposed over large areas, and vegetation is rare or absent. Physical erosion is rapid due to glaciation, mass wasting, and torrential rain events. Chemical weathering is minimal and sulphide minerals commonly crop out at the surface, largely unoxidised.

Epithermal deposits of the Coromandel Peninsula and Northland are exposed to a warm temperate to sub-tropical climate. Elevated topography due to active or Recent faulting, combined with ocean proximity, results in high rainfall (2000–3000 mm/year). The active tectonics and high rainfall ensure steep topography, which is mantled by forest. Underlying rocks are deeply weathered in Northland where most rocks have been altered to clay for at least 10 m below surface and variable degrees of oxidation persist to more than 30 m. Forest soil pH is typically near 5 in this setting. This style of clay weathering is less pronounced in the Coromandel area due to higher relief and greater erosion. Hence, some nearly fresh rock is exposed in Coromandel valleys, primary and secondary calcite is preserved, and forest soil pH is near 7.

5.2. Geochemical methods

Field pH was determined with an Oakton WD 35615 field pH meter calibrated regularly with standard solutions. Solid material was analysed by X-ray fluorescence in the Geology Department, University of Otago using techniques and standards as described by Craw et al. (2000a). Water samples were collected in acid-washed plastic bottles and filtered before analysis. Some water samples were collected as stream-bed slurries, and pore water was extracted from the slurries by centrifuge and filtered before analysis. Chemical analyses were conducted by Chemsearch (University of Otago Chemistry Department), an internationally accredited laboratory, using atomic absorption spectrophotometry (AAS). Additional water analyses were provided by GRD Macraes Ltd, the operators of the Macraes mine (Fig. 2B), from their on-going monitoring programme. These analyses also were conducted by Chemsearch. Some water analyses from Coromandel Peninsula were provided by Waihi Gold, operators of the Martha mine (Fig. 2A). Additional Coromandel analyses were obtained from Carter (1983), Beaumont et al. (1987), Pang (1995), and unpublished mine planning documents for the Monowai mine.

Mercury is a difficult element to sample and analyse accurately in the field context due to its volatility. Also, high rainfall ensures that mercury is quickly diluted in the Coromandel and Northland epithermal area examined in this study. Hence, mercury mobilisation data have not been compiled for the natural environment, and experimental leaching of mercury from natural samples was undertaken. Cinnabar-rich material was not examined because of the known low solubility of cinnabar in the natural environment (Hem, 1970). Samples of variably oxidised mineralised zones from Puhipuhi were selected because mercury is present in minerals other than cinnabar (Craw et al., 2000b). Samples were leached in two different sulphuric acid solutions (pH 1, and 50% concentrated sulphuric acid) in closed containers for various times up to 440 h, and resultant solutions were analysed for mercury by AAS using flow-injection mercury/hydride method. Detection limit for the technique is 5 ppb dissolved Hg.

5.3. Maximum potential acidity

Maximum potential acidity (MPA) is a measure of the potential production of sulphuric acid from breakdown of sulphides during oxidation. Pyrite is the most significant contributor to acid generation, via a complex series of reactions which can be summarised:

$$FeS_2 + (7/2)O_2 + H_2O = Fe^{++} + 2SO_4^{--} + 2H^+$$

(Garrels and Thompson, 1960)

Consequently, MPA can be calculated from the percentage of sulphide sulphur in the rock (Hutchison and Ellison, 1992). This can be expressed as potential amount of acid produced, or as an equivalent amount of calcium carbonate (calcite) required to neutralise the sulphuric acid. The later expression is used in this paper to facilitate comparison with acid neutralisation capacity (Section 5.4).

5.4. Acid neutralisation capacity

Acid neutralisation capacity (ANC) is a measure of the capacity of a rock to neutralise sulphuric acid generated by sulphide decomposition and these acid neutralisation reactions are dominated by calcite decomposition (Hutchison and Ellison, 1992). Some micaceous minerals can also contribute to neutralisation. Chlorite is the most likely mineral to be involved in such reactions because it is more reactive at ambient temperatures than, for example, muscovite (Craw, 2000). Clay minerals, especially kaolinite, have negligible neutralisation effect.

ANC can be determined by a standard laboratory test (Sobek et al., 1978) and as such is empirical rather than theoretical like MPA. The results of the laboratory test are generally expressed in terms of equivalent calcium carbonate content, to acknowledge that calcite is the most important neutralisation mineral, and to facilitate comparison with MPA (see above).

6. Acid rock drainage

6.1. MPA vs ANC in mesothermal and epithermal mineralised areas.

Large amounts of data are available on MPA and ANC from Otago and Coromandel Peninsula because of the presence of large modern mines (e.g. Martha Fig. 2A; Macraes, Fig. 2B) with active environmental programmes. While the mines all have local geological characteristics, they provide some insight into the general nature of rocks in their respective regions. Comparative data compiled from a wide variety of sources are depicted in Fig. 3A. This shows the clear contrast in the potentials for acidification in the two areas. These two areas are representative of the principal tectonic settings present in New Zealand: mesothermal deposits formed by continental collision (Macraes) and epithermal deposits formed associated with calcalkaline are magmatism (Coromandel).

Otago MPA vs ANC data, focussed on the Macraes mine, show that the ANC is generally high except in weathered rocks, and greatly exceeds the MPA of the ore. This pattern reflects the fact that Otago Schist contains calcite and chlorite as prominent minerals in almost all rocks. These latter minerals decompose under weathering conditions. Mineralised rock generally contains only 1–2% sulphide minerals, which is commonly overshadowed by an additional carbonate mineral component introduced during mineralisation. This is typical of continental collision-related mesothermal systems in New Zealand.

In contrast, Coromandel rocks have generally low to moderate ANC (Fig. 3A) due to their low calcite content. The highest calcite contents occur in propylitically altered rocks and locally in veins. Most ore contains little calcite. Chlorite in propylitically altered rock also contributes to the ANC, but chlorite was destroyed by more intense alteration around vein systems. The low to moderate ANC is overshadowed by generally high MPA (Fig. 3B) which arises from the high pyrite content of most altered rock and other sulphides in the main mineralised zones. Thus, the typically low ANC and high MPA of these deposits reflect the high degree of hydrothermal alteration characteristic of the meteoric water-dominated epithermal systems of the calcalkaline arc environment of the North Island.

Variations in ANC (estimated from carbonate) and MPA with distance from a mineralised vein system at the Tui mine (Fig. 2A) mirror the degree of alteration of the host rock (Fig. 3B). In general, MPA increases towards the vein system, and ANC increases away from the vein system except where calcite has been added in veins. The locally substantial excess of MPA over ANC results in acid mine drainage (Pang, 1995). In contrast, the Maratoto mine (Fig. 2A) is hosted in predominantly propylitically altered rock and ore contains abundant calcite (Craw and Chappell, 2000). Hence, ANC is high compared to most Coromandel rocks, and MPA is average to low (Fig. 3A). Water in 40-year old Maratoto mine tailings has pH between 7 and 8.5 (Craw and Chappell, 2000), attesting to the high ANC in these less-altered rocks.

6.2. Natural groundwater acidity in epithermal deposits

The high MPA of Coromandel ore zones is a well-recognised potential environmental problem during mining operations (Carter, 1983; Beaumont et al., 1987; Pang, 1995). However, this high MPA is a natural phenomenon which contributes to low groundwater pH in mineralised rocks. Coromandel groundwater is generally strongly diluted by surface waters in this high rainfall setting (above). Acid groundwater occurs in some old mine adits, but these are affected by oxidation of sulphides in the adit walls (Craw and Chappell, 2000). Only under near-drought conditions are natural groundwater seepages apparent, and can be measured undiluted. Data for the following acid examples were collected in a period of low rainfall (June) after the dry El Nino summer of 1997–98. Groundwater in incipiently propylitically altered rock, which dominates most catchments, has near-neutral pH, which translates into near-neutral stream waters under low-flow conditions.

Groundwaters from Una Hill above Thames (Fig. 2A), show a wide range in pH which reflects the underlying rock alteration pattern (Fig. 4). These waters are from natural seeps in a mineralised area whose old mine adits occur mainly in the unsaturated zone. One sample of groundwater was taken from an adit in the propylitic zone, but nearby seeps also had the same neutral pH. The low pH in the more altered rocks reflects natural acidification of the groundwater

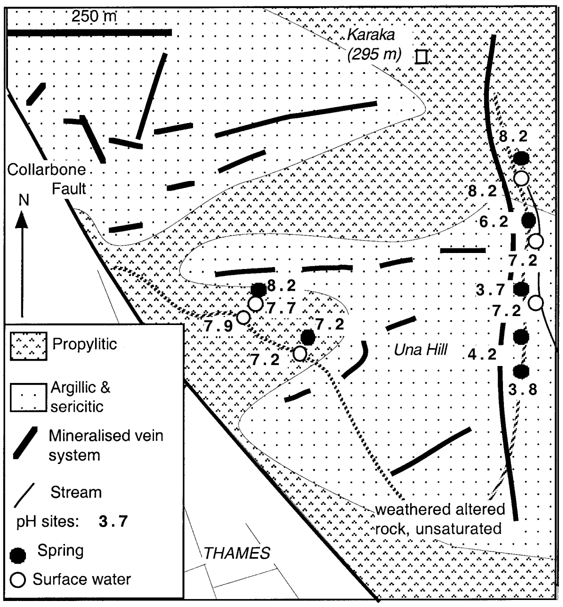

Fig. 4. Geological map of an epithermal mineralised zone near Thames (Coromandel Peninsula, Fig. 2A), showing locations of mineralised veins and associated alteration zones (partly from Fraser, 1910 and Merchant, 1986). The pH of groundwater springs, and surface water derived from groundwater springs, is indicated (after Craw and Chappell, 1998). Access track is hatched.

as expected from the measured MPA data for such altered rocks. Groundwater seepages emanate from a quarried mineralised zone in the Waiotahi Valley near Thames (Fig. 2A), with pH near 2 (Fig. 5A) reflecting the high oxidising pyrite content of the altered underlying rocks. These seepages flow over pyrite-bearing rocks at the surface with little change in pH (Fig. 5A). Downstream dilution by stream water results in neutralisation (Fig. 5B).

A spring emanating from a hillside beside the road to the historic Monowai mine (Fig. 2A) has pH near 2. The immediately adjacent rocks are propylitically altered, but more intensely altered rocks occur within, and higher up, the hillside (Skinner, 1993). The spring does not issue from old mine workings, but is clearly affected by the sulphide content of the altered rock nearby.

All rocks in Northland are deeply weathered to clays in the upper 10 metres or more, and primary calcite has been leached. In addition, hydrothermal alteration has further decomposed primary rocks to clays or silicified zones, again with negligible calcite. Hence, the Northland rocks have little or no natural acid neutralisation capacity. Oxidation of iron sulphides in mineralised zones inevitably results in acid water discharge. Seeps from mineralised zones typically have pH between 3 and 4. One 3 m high quarry wall in a historic mercury mine has seeps with pH between 1 and 2 (Fig. 6A). This low pH is capable of leaching metals from the mineralised rocks (Fig. 6B; see below). This acid water has pH rise downstream due to mixing with seeps and streams with slightly higher pH (Fig. 6A). However, the pH remains below 5 for long distances (kilometres) because of the lack of neutralising capacity in the underlying rock.

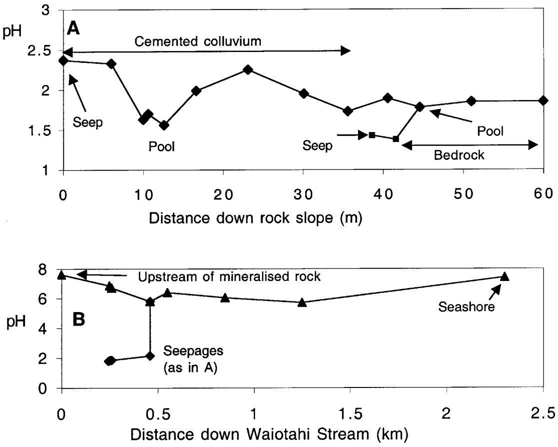

Fig. 5. Changes in pH downstream in water catchments in an epithermal mineralised area, Waiotahi Stream near Thames (Fig. 2A). (A) Small scale variations of pH as springs seep from pyritised rock in an argillically altered zone exposed in a quarry, and flow over colluvium and bare rock. (B) Larger scale pH variations in the main Waiotahi Stream as it flows from propylitically altered headwaters past the site in A and down to the sea.

6.3. Natural groundwater in Otago mesothermal deposits

Otago Schist groundwater almost invariably has neutral or alkaline pH, reflecting the significant calcite content of the host schist. Even sulphide-rich mineralised rocks rarely affect the pH by more than 1 unit. A cross section from underlying schist into a mineralised 100 m thick shear zone at Macraes (Figs. 2B and 7A) shows that there is very little change in pH towards the sulphide-bearing zone. The most variable

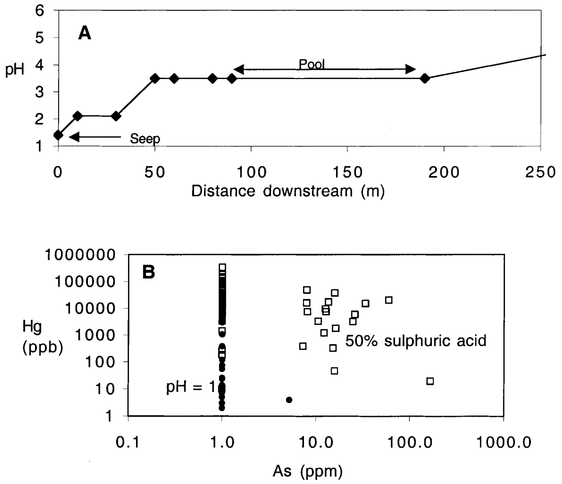

Fig. 6. Environmental chemistry of variably mineralised rock associated with epithermal mercury mineralisation at Puhipuhi, northern North Island (Fig. 1). (A) Changes in water pH downstream from a groundwater spring seeping from a quarry in a siliceous cinnabar-rich zone with pyrite and marcasite, as the water flows over forest-covered deeply clay-weathered greywacke bedrock with background pH near 5, which is reached 200 m downstream of this diagram (Craw et al., 2000b). (B) Dissolved arsenic and mercury contents of solutions derived from laboratory experiments in which variably oxidised rocks from Puhipuhi mineralised zones were subjected to leaching by pH = 1 sulphuric acid solutions (black circles), and solutions made from 50% concentrated sulphuric acid and 50% distilled water (open squares). Analytical detection limits for these experiments were 1 ppm As and 5 ppb Hg.

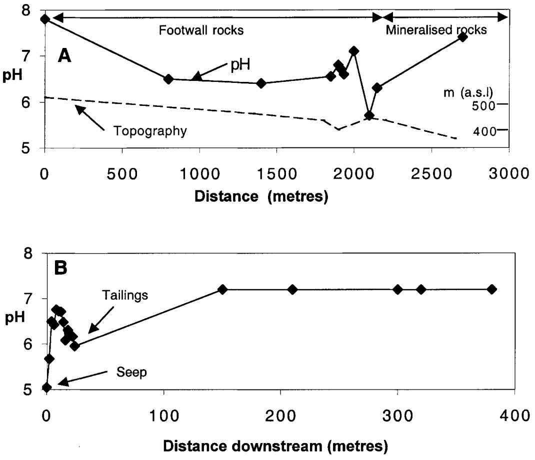

Fig. 7. Changes in water pH in the vicinity of oxidised mineralised rock from mesothermal zones in Otago (Fig. 1). (A) The pH of groundwater in boreholes in a traverse into the mineralised zone at the Macraes mine (Fig. 2B), in relation to the topographic surface (dashed line). (B) Variation of surface water pH downstream from where a groundwater spring emanates from a mineralised zone at Barewood (Fig. 2B; Craw et al., 2000a) and flows past 90-year old oxidised mine tailings.

portions of this section involve waters in locally mineralised host rock on a small topographic high (Fig. 7A). Groundwater is so strongly compartmentalised by fracture permeability that there is little physical or chemical connection even at the scale of metres on this topographic high. The semi-arid climate ensures that little flushing of the groundwater system occurs.

A seep emanating from a mineralised zone at Barewood in east Otago (Fig. 2B) has pH near 5 (Fig. 7B) due to oxidation of sulphide minerals in a 2–3 m wide quartz vein with no calcite. However, the pH rises to 7 immediately downstream of the mineralised zone (Fig. 7B). The pH of the same watercourse decreases downstream again to below 6 as water passes through some historic mine tailings, then rises again to 7 (Fig. 7B).

Mesothermal deposits in the tectonically active Southern Alps continental collision zone are regularly flushed with rain water as moist westerly winds move over the mountains and release their moisture. This regular flushing, combined with the high carbonate contents of the host rocks and veins, ensures that no acid rock drainage results during the incipient oxidation of the deposits that occurs before physical erosion of the mountains.

7. Chemical mobility of metals

7.1. Arsenic

Acidification can lead to mobilisation of metals, either naturally or in a mine operation situation. Mesothermal mineralised rocks have relatively simple mineralogy, and arsenic is the largest potential environmental problem (Fig. 8A). Base metals (Cu, Pb, Zn) are not enriched, and only small amounts are available for mobilisation (Fig. 8A and B). In epithermal gold mineralised zones, base metals are generally enriched (Fig. 8A and B) and these are the most likely metals to be mobilised. Arsenopyrite is rare but arsenic is present in solid solution in many of the sulphides, and in accessory arsenic minerals.

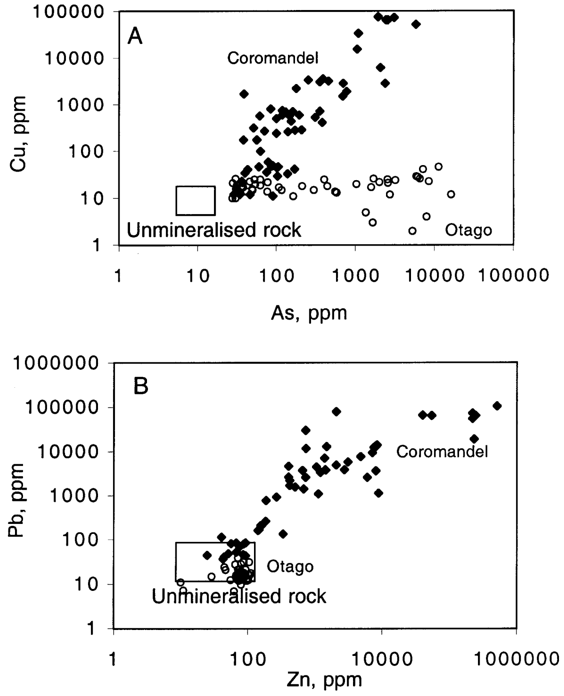

Fig. 8. Comparison of metal contents of mineralised and unmineralised rocks in epithermal (Coromandel; black diamonds) and mesothermal (Otago; open circles) deposits, indicating principal enrichments associated with mineralisation in the two different settings. Note the logarithmic scales on all axes. (A) Arsenic and copper contents. (B) Zinc and lead contents.

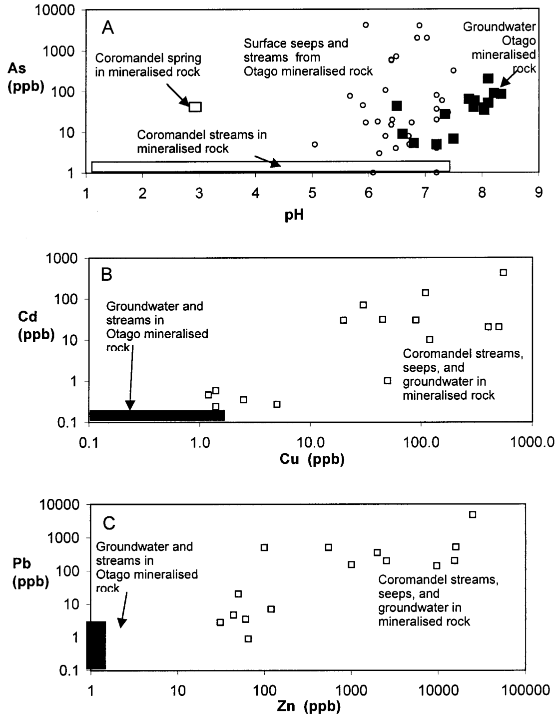

Fig. 9. Chemistry of surface and ground waters in the vicinity of mineralised zones in the Coromandel Peninsula area (epithermal) and east Otago area (mesothermal). (A) Water pH and dissolved arsenic content of groundwater in mineralised rock at Macraes mine (black squares) and surface springs and nearby streams in Otago (open circles), compared to Coromandel waters in mineralised rock (range shown by boxes). (B) Dissolved copper and cadmium contents of Coromandel waters (open squares) compared to Otago waters (range shown with black box). (C) Dissolved zinc and lead contents of Coromandel waters (open squares) compared to Otago waters (range shown with black box).

The most stable oxidised arsenic mineral is scorodite, $FeAsO_4 \cdot 2H_2O$, which can form during oxidation of arsenic-bearing sulphides. Scorodite solubility is strongly controlled by pH: it is soluble at low pH, decreases solubility to a minimum at about pH 4, then steeply increases solubility again (Krause and Ettel, 1988). Scorodite is extremely soluble under neutral–alkaline conditions (hundreds to thousands of ppm As in solution). Hence, there is a narrow pH range, ca. 4 ± 1, in which scorodite can be considered a useful mineral for fixation of environmental arsenic. Outside this range, arsenic is readily mobilised into the environment. Thus, the lack of acidification of groundwater in Otago mineralised areas (Fig. 7A and B) means that As is highly soluble, and some high levels of As can be detected in natural waters (up to 4 ppm, Fig. 9A). Elevated dissolved As is characteristic of the mesothermal setting of southern New Zealand.

Conversely, natural acidification of groundwaters in the Coromandel ensures that As is almost always insoluble in sulphide oxidation zones, and As levels in Coromandel waters are low (Fig. 9A). Hence, the wet acid epithermal terranes of the North Island are generally characterised by low dissolved As. One exception is the spring near the Monowai mine (above; Fig. 2A), which has ca. 30 ppb dissolved As at pH near 3 (Fig. 9A), despite evidence for adsorption and/or mineral formation in association with iron oxyhydroxides at that site (Craw and Chappell, 2000).

7.2. Base metals

Copper released from oxidising sulphides or from processing effluent can be fixed at near-neutral or alkaline pH as copper hydroxides, oxides, or carbonates (Garrels and Christ, 1965; Du et al., 1997), or as adsorbed complex on clay minerals (Du et al., 1997). Under more acidic conditions, copper is released from all these sites into solution. Hence, Cu is mobilised in epithermal settings such as Coromandel acidic sulphide oxidation zones (Fig. 9B). Cadmium responds in a similar way to copper, and is mobilised in epithermal sites (Fig. 9B). Neither copper nor cadmium are mobilised in mesothermal settings such as in Otago sulphide oxidation zones (Fig. 9B). Lead and zinc behave in a similar way to copper and cadmium, but are distinctly more soluble in the oxidising epithermal environment of the Coromandel area (Fig. 9C). Again, there is no mobilisation of these metals in the Otago mesothermal setting (Fig. 9C).

Anomalous concentrations of antimony are present in many deposits in all tectonic settings (above). Few data are available on Sb mobility in New Zealand, although thermodynamic calculations predict that Sb solubility on oxidation is similar to that of arsenic under alkaline to moderately acid conditions (Vink, 1996). Because Sb is only a minor component of hydrothermal systems addressed in this paper, it is considered beyond the scope of the present work.

7.3. Mercury

Mercury in Northland primary mineralised sites is present mainly in cinnabar, which remains undissolved in sedimentary deposits as old as Pliocene (Henderson, 1944). Minor mercury occurs in solid solution in marcasite and hydrothermal phosphate minerals (Craw et al., 2000b). Marcasite readily decomposes during oxidation, and the stability of the phosphatic material is not known. Mercury released from decomposing marcasite is commonly adsorbed temporarily on or in iron oxyhydroxides (Craw et al., 2000b). This adsorbed mercury can be leached from variably oxidised mineralised rock with dilute sulphuric acid solutions ($\mathrm{pH} = 1$) or 50% sulphuric acid (Fig. 6B). The dilute acid solution is representative of water occurring in the field (Fig. 6A). Marcasite also contains minor arsenic (Craw et al., 2000b) and this is released to iron oxyhydroxides during oxidation as well. The arsenic is not leached by dilute sulphuric acid, but is readily leached by 50% sulphuric acid solution (Fig. 6B). These experiments suggest that mercury from marcasite will readily discharge to the environment from some epithermal sites, but associated arsenic remains more tightly bound during oxidation.

Mesothermal mercury deposits in Otago release cinnabar to form a detrital component of river sediments, where it accumulates with heavy mineral fractions, including gold, in placer deposits (Youngson et al., 2001). The cinnabar is chemically stable on the human time scale but minor chemical etching of detrital grain surfaces suggests that some dissolution may occur on geological time scales. Mercury occurs in gold as natural amalgams in some placer deposits, presumably derived from cinnabar vein systems, and this mercury is leached from the alluvial gold on geological time scales (Youngson et al., 2001).

8. Conclusions

Metallic mineralisation in the New Zealand orogen is related to tectonic setting. The tectonic setting also affects topography and climate. Consequently, environmental impacts of mineral deposits are broadly related to tectonic setting. Epithermal gold deposits associated with calcalkaline arc magmatism in a warm temperate climate are characterised by regional scale propylitic host rock alteration with more local sericitic and argillic alteration and extensive pyritisation (Fig. 10A). Pyrite oxidation causes acid rock drainage in the mineralised zone and elevated dissolved copper, cadmium, lead and zinc is discharged in low pH water which is neutralised on the kilometre scale (Fig. 10A). Epithermal mercury deposits associated with extension-related mantle-derived basaltic volcanism in a subtropical climate have more localised alteration haloes (10 m scale). Iron sulphide decomposition results in acid rock drainage which is not neutralised by the deeply clay-weathered host rock (Fig. 10B). Mercury is mobilised in the acid waters from marcasite and phosphate minerals but not from cinnabar.

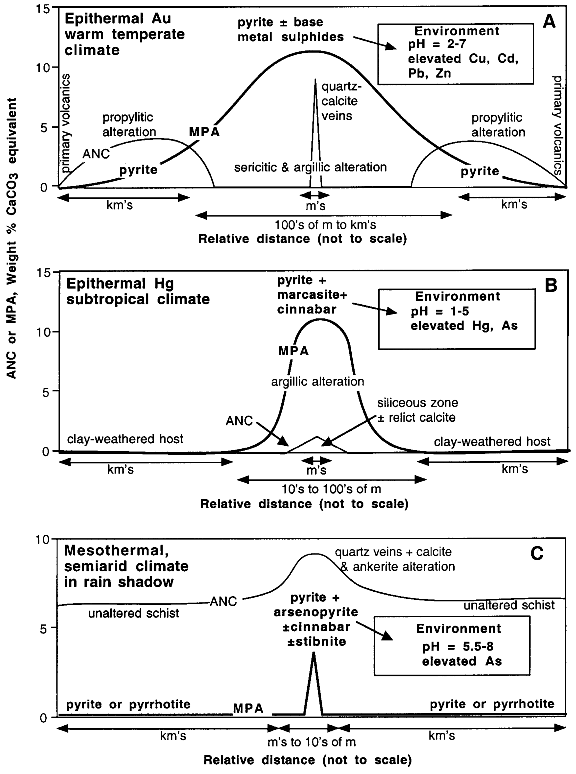

Fig. 10. Schematic diagrams showing the relative magnitudes of acid neutralisation capacity (ANC) and maximum potetial acidity (MPA) with distance across typical mineral deposits in different tectonic settings and climates, showing typical environmental impacts which result. (A) Epithermal gold deposits formed associated with calcalkaline magmatism above a subduction zone and exposed to a warm temperate climate, such as Coromandel Peninsula. (B) Epithermal mercury deposits formed associated with continental extensional basaltic magmatism and exposed to deep subtropical weathering, such as northern New Zealand. (C) Mesothermal gold deposits formed during continental collision and exposed to a cool semiarid climate, such as Otago.

Mesothermal deposits formed in a continental collision setting now occur in a tectonically created rain shadow in a cool semiarid climate. High carbonate content of host rock and mineralised zones prevents significant acidification during oxidation of minor sulphides (Fig. 10A). Decomposition of arsenopyrite releases arsenic which is relatively soluble in the alkaline waters typical of this environment. Hence, As mobility, rather than acid drainage, is the most important environmental issue around such mesothermal mineralised zones.

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