

# 11. Hydrothermal Alteration

By W.C. Pat Shanks III

11 of 21

## **Volcanogenic Massive Sulfide Occurrence Model**

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# 11. Hydrothermal Alteration

By W.C. Pat Shanks III

The geochemical reactions that produce hydrothermal alteration in host rocks of VMS deposits are critically important for a number of reasons. First, three-dimensional distributions of hydrothermal alteration zones are produced by circulating hydrothermal fluids and thus provide evidence for pathways of fluid travel and geochemical evidence for the physical and chemical conditions of alteration. The chemical and mineralogical distributions of hydrothermal alteration zones are generally the only direct evidence of fluid circulation patterns related to VMS ore formation. Second, systematic arrangement of hydrothermal alteration zones, and recognition of this arrangement, may provide information useful in mineral exploration and may in some cases provide vectors to undiscovered deposits. Third, hydrothermal alteration can provide key information on the origin of metallic elements in VMS deposits. For example, depletion of key elements in altered rocks, combined with measured or inferred estimates of the volume of altered rock, can constrain possible sources of ore metals. Finally, identification and recognition of hydrothermal alteration assemblages and their zonal relationships in the field may provide important evidence that a terrane under assessment is favorable for occurrence of VMS deposits.

Hydrothermal alteration varies widely from district to district and among individual deposits, and the literature on this topic is voluminous. A detailed review is beyond the scope of this report; the interested reader is referred to the following summary references and additional citations therein: Slack (1993), Ohmoto (1996), Carvalho and others (1999), Galley and Koski (1999), Large and others (2001a), Herrington and others (2003), Gifkins and others (2005), Peter and others (2007), Galley and others (2007), Gibson and Galley (2007), and Goodfellow (2007).

Fortunately, alteration zones related to VMS deposits do show characteristic zonal arrangements (proximal, distal, comformable) that may be related to fluid flow and water/rock interaction processes (upflow, recharge, burial metamorphism). In addition, fairly standard alteration assemblages, defined by alteration mineralogy, also occur in country rocks around many deposits, and even metamorphosed alteration zones produce predictable assemblages.

## Relations among Alteration, Gangue, and Ore

Ore is traditionally defined as a valuable mineral or chemical commodity that can be extracted at a profit. In VMS deposits, ore generally consists of sulfide or sulfosalt minerals that contain Cu, Pb, Zn, Ag, and (or) Au. Gangue is defined as any noneconomic mineral deposited together with ore; in VMS deposits this means essentially all nonsulfide minerals (see “Hypogene Gangue Characteristics,” Chapter 9, this volume) and some hydrothermal sulfide minerals (typically pyrite or pyrrhotite) that lack economic value. Hydrothermal alteration is defined as any alteration of rocks or minerals by the reaction of hydrothermal fluid with preexisting solid phases. Hydrothermal alteration can be isochemical, like metamorphism, and dominated by mineralogical changes, or it can be metasomatic and result in significant addition or removal of elements. Where alteration is intense, it can result in significant volume changes such that mass balance approaches using immobile elements are required to fully understand the alteration process (Gresens, 1967).

Some authors include gangue and hydrothermal alteration together (Beane, 1994) but, in the context of VMS deposits, it seems useful to continue distinguishing gangue from alteration. Alteration is by definition an epigenetic process that modifies preexisting rocks (or sediments), whereas gangue is generally a syngenetic mineral deposited on or near the seafloor along with the ore minerals. However, distinctions between gangue and alteration become difficult in cases where VMS mineralization occurred by replacement and open space filling in porous and permeable rocks in shallow zones beneath the seafloor.

In some cases, the bulk of the massive sulfide ore may be deposited in shallow subseafloor environments. In this mode of mineralization, hydrothermal fluids flow into highly permeable, high-porosity rocks, where sulfide precipitation is triggered by mixing with cold ambient seawater in the pore space. The prime example of this style of mineralization is the giant Kidd Creek deposit, where most mineralization occurred below the seafloor in permeable, fragmental felsic volcanic

rocks by infill and replacement (Hannington and others, 1999). A similar origin is inferred for the Horne mine (Kerr and Gibson, 1993), the Ansil deposit where laminated felsic ash flows/turbidites were replaced by sulfides and silica (Galley and others, 1995), and for the Turner-Albright ophiolitic deposit where massive sulfide formed below the seafloor within basaltic hyaloclastite (Zierenberg and others, 1988). Hannington and others (1999) suggested that subseafloor mineralization also formed some of the Bathurst (New Brunswick) deposits.

## Mineralogy, Textures, and Rock Matrix Alteration

Hydrothermal alteration of volcanic host rocks involves the replacement of primary igneous glass and minerals (plagioclase, orthoclase, quartz, biotite, muscovite, amphibole, pyroxene, titanomagnetite) with alteration minerals stable at the conditions of alteration, generally in the temperate range of 150–400 °C. Alteration minerals in unmetamorphosed lithologies may include quartz and other forms of silica (chalcedony, opal, amorphous silica), illite, sericite, smectite, chlorite, serpentine (lizardite, chrysotile), albite, epidote, pyrite, carbonates, talc, kaolinite, pyrophyllite, sulfates (anhydrite, barite, alunite, jarosite), and oxides (magnetite, hematite, goethite). These hydrothermal alteration minerals may be transformed during metamorphism into andalusite, corundum, topaz, sillimanite, kyanite, cordierite, garnet, phlogopite, and various orthopyroxenes and orthoamphiboles (Bonnet and Corriveau, 2007).

Alteration textures range from weak alteration of only some of the minerals or matrix in the host rocks, producing a punky or earthy aspect to the overall rock, or to partially-altered phenocrysts. Such alteration may be difficult to distinguish from weathering in the field. Glassy rock matrix or fine-grained mesostasis can be particularly susceptible to alteration and may be massively silicified or replaced by chlorite or sericite as alteration intensity increases. At high alteration intensity, rocks may be pervasively altered, in which virtually all primary phases in the rock are altered to new hydrothermal minerals. In the extreme case of stringer zones immediately underlying massive sulfide deposits, it is not unusual to find massively altered rock that consists of quartz, chlorite, and chalcopyrite veins, with or without lesser amounts of pyrite, sericite, and carbonates. Stringer zone rocks may be unrecognizable in terms of original lithology.

Occasionally rock alteration leads to misidentification of lithology as in studies of the Amulet rhyolite in the Noranda district. Lithochemical studies using immobile element patterns have shown that the Upper Amulet rhyolite is actually a hydrothermally altered andesite-dacite (Gibson and others, 1983; Barrett and MacLean, 1999). Similarly, in the intensely silicified zones at the Turner-Albright VMS deposit, basaltic hyaloclastite has been progressively replaced by quartz-sericite-chlorite, quartz-chlorite, and finally quartz-sulfide

(Zierenberg and others, 1988). The completely silicified rocks were originally mapped as “chert exhalite,” but careful mineralogical, geochemical, and isotopic studies showed the presence of relict igneous chromium spinel, proving massive hydrothermal replacement. Similar extreme alteration has been documented locally in the amphibolite-facies wall rocks to the Elizabeth VMS deposit, Vt., where assemblages such as quartz-white mica-calcite and quartz-white mica-albite-staurolite-garnet-corundum contain uniformly high Cr/Zr and Ti/Zr ratios, which reflect protoliths of tholeiitic basalt that were pervasively metasomatized during seafloor hydrothermal mineralization (Slack, 1999; Slack and others, 2001).

These studies underscore the importance of understanding the nature and effects of hydrothermal alteration in VMS systems, including overprinting by postore regional metamorphism.

## Mineral Assemblages and Zoning Patterns

Early studies of alteration mineral assemblages emphasized zonal arrangements of mineralogy around sulfide veins at Butte, Mont. and at several porphyry copper deposits (Sales and Meyer, 1948; Titley and Hicks, 1966; Meyer and Hemley, 1967; Meyer and others, 1968). Studies of alteration assemblages in these continental hydrothermal settings led to a series of commonly recognized alteration zones: potassic, argillic, phyllic, and propylitic, with distinct mineralogy and decreasing intensity of alteration developed away from the vein or pluton, respectively. Bonnet and Corriveau (2007) retained some of these classification terms (table 11–1) and used some of the assemblage names for VMS deposits, but substituted sericitic for phyllic and, like other researchers, added chloritic as an important alteration zone in subseafloor settings. Advanced argillic is a special type of alteration that forms in highly acidic, high sulfidation-state conditions characteristic of near-seafloor (or near-surface) oxidation of SO<sub>2</sub> or H<sub>2</sub>S to produce sulfuric acid.

Experimental and theoretical geochemical studies (Hemley and Jones, 1964; Beane, 1994; Reed and Palandri, 2006) have established a firm thermodynamic basis for the occurrence of these hydrothermal alteration assemblages. Studies of metamorphosed VMS deposits have clearly shown that the primary alteration minerals are transformed into predictable higher temperature and pressure mineral assemblages (table 11–1) (Bonnet and Corriveau, 2007).

## Alteration in Modern Seafloor Volcanogenic Massive Sulfide Systems

Subseafloor VMS hydrothermal alteration zoning is less studied than equivalent systems on the continents because of the primitive level of exploration and relative paucity of drilling, but such zoning is important because the deposits have

**Table 11–1.** Diagnostic minerals in hydrothermally altered volcanogenic massive sulfide deposits at different metamorphic grades.

[Modified from Bonnet and Corriveau, 2007. Fe, iron; K, potassium; Mg, magnesium]

Alteration type	Diagnostic minerals: unmetamorphosed deposits	Diagnostic minerals: greenschist facies	Diagnostic minerals: granulite facies
Advanced argillic	Kaolinite, alunite, opal, smectite	Kaolinite, pyrophyllite, andalusite, corundum, topaz	Sillimanite, kyanite, quartz
Argillic	Sericite, illite, smectite, pyrophyllite, opal	Sericite, illite, pyrophyllite	Sillimanite, kyanite, quartz, biotite, cordierite, garnet
Sericitic	Sericite, illite, opal	Sericite, illite, quartz	Biotite, K-feldspar, sillimanite, kyanite, quartz, cordierite, garnet
Chloritic	Chlorite, opal, quartz, sericite	Chlorite, quartz, sericite	Cordierite, orthopyroxene, orthoamphibole, phlogopite, sillimanite, kyanite
Carbonate propylitic	Carbonate (Fe, Mg), epidote, chlorite, sericite, feldspar	Carbonate (Fe, Mg), epidote, chlorite, sericite, feldspar	Carbonate, garnet, epidote, hornblende, diopside, orthopyroxene

not experienced significant deformation or metamorphism. Several areas on the seafloor have provided enough information to begin to understand alteration mineralogy and chemistry and the spatial arrangement of alteration types related to VMS systems: the Galapagos Rift stockwork zone, mafic systems at TAG, a siliciclastic mafic system at Middle Valley, and a bimodal felsic system in Manus Basin north of Papua New Guinea (fig. 11–1).

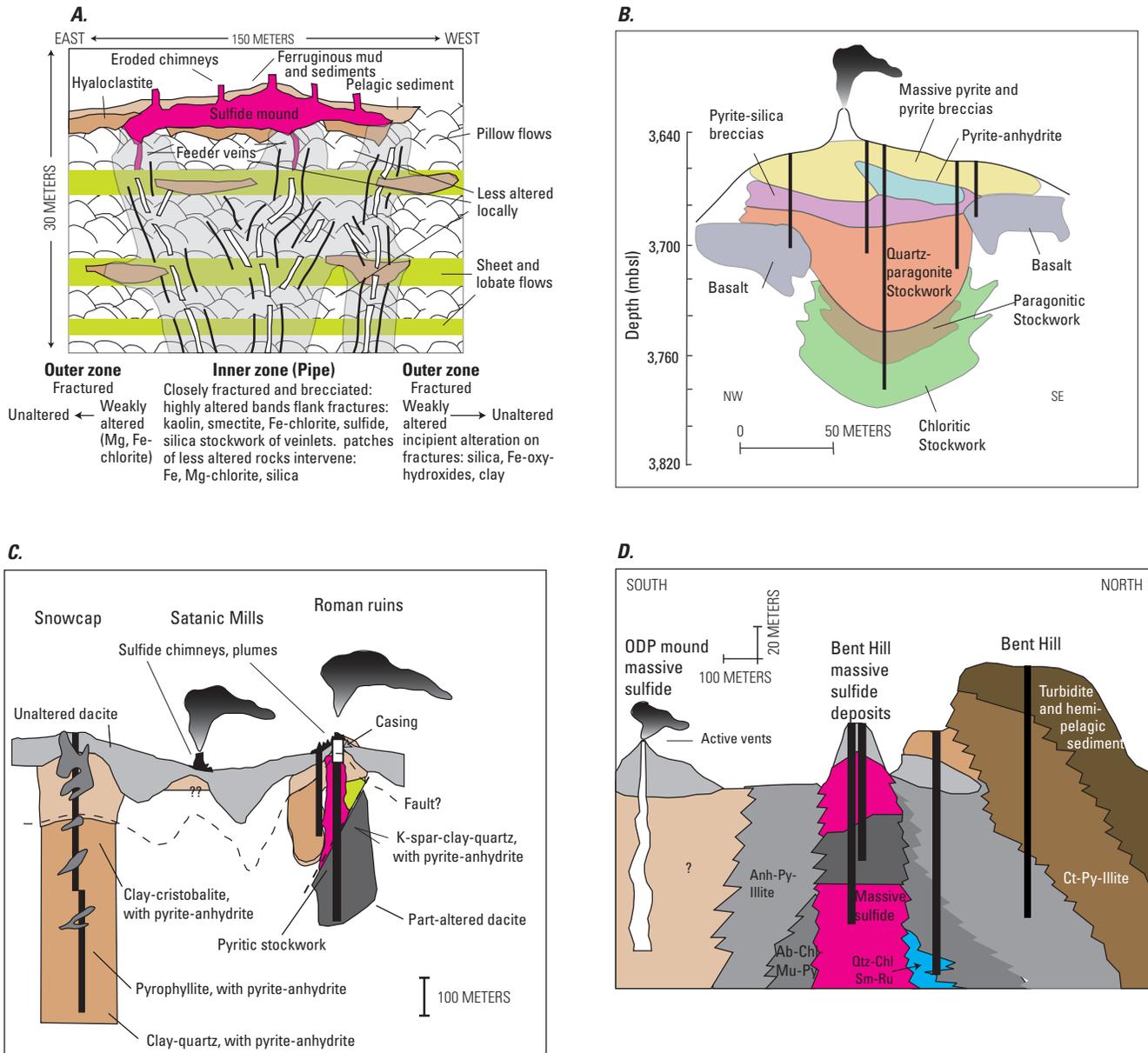
A remarkable stockwork alteration zone has been studied at the Galapagos Rift beneath a presently inactive sulfide mound where a host block provides outcrop exposure (fig. 11–1A) (Embley and others, 1988; Ridley and others, 1994). The inner zone of the stockwork in basaltic pillows, lava flows, and hyaloclastite contains sulfide veins and Fe-rich chlorite-smectite-kaolinite-quartz alteration of selvages and host rocks. Peripheral to the inner zone, alteration is weak and dominated by Mg-rich chlorite, clays, iron oxides, and silica.

Studies by ODP drilling of the TAG VMS mound on the Mid-Atlantic Ridge (fig. 14–1B) emphasize seafloor precipitation and remobilization of hydrothermal sulfide and sulfate minerals and provide a crude picture of alteration zoning in the host rocks beneath TAG. Basically, the stockwork zone immediately beneath the deposit is a silicified, pyritic wallrock breccia with minor paragonite (also referred to as sericite) that increases with depth in this zone. Beneath, and to some extent surrounding, the stockwork zone is a chloritized basalt breccia that consists primarily of chlorite-quartz-pyrite with minor hematite, and smectite and talc in the altered rock matrix (Honnorez and others, 1998). Drilling did not penetrate deeper into basement and the expected peripheral sericitic and propylitic alteration zones were not encountered.

Manus Basin, where dacite-dominated (andesite to rhyodacite) lava flows and hydrothermal vents occur on Paul

Ridge, was drilled during ODP Leg 193 to a maximum depth of 387 m (Binns and others, 2007). Three holes penetrated hydrothermally altered rocks (fig. 11–1C). Most of the alteration is represented by clays plus silica. Silica occurs as opal-A in near-surface rocks, with progressive transition to cristobalite and then quartz with depth. Clays are chlorite, illite, and mixed-layer phases including chlorite, smectite, illite, and vermiculite (Lackschewitz and others, 2004). Pyrophyllite occurs in patches and is believed to be related to acid-sulfate alteration. Beneath the Roman Ruins hydrothermal vent area, there are a well-developed pyrite-quartz-anhydrite stockwork and an unusual K-feldspar alteration zone. Zonation is not particularly systematic at this site, and is somewhat different than that at most ancient massive sulfides, but may well represent precursor alteration zones to those defined in lithified or metamorphosed rocks.

Alteration related to the Middle Valley hydrothermal system provides a good example of altered sediment and basalt in a siliciclastic-mafic system (fig. 11–1D). Goodfellow and Peter (1994) found well-defined alteration zones from ODP Leg 139 drilling in the sedimentary host rocks around the massive sulfide deposit at Bent Hill. Alteration facies range from a deep inner zone of quartz-chlorite-smectite-rutile, outward to albite-chlorite-muscovite-pyrite, anhydrite-pyrite-illite, and calcite-pyrite-illite. These zones may roughly correspond to an inner chloritic zone and an outer sericitic (illitic) zone, with the calcite-pyrite zone showing similarities to propylitic alteration (table 11–1). ODP Leg 169 (Zierenberg and others, 1998) deepened and widened drill coverage in and around the Bent Hill massive sulfide deposit (see fig. 3–2B, this volume). In particular, deepening of Hole 856H penetrated 107 m of a sulfide feeder zone within altered turbidites beneath the massive sulfide, 221 m of interbedded turbidites and pelagic



**Figure 11–1.** Representative cross sections of alteration related to hydrothermal activity or fossil hydrothermal activity on the modern seafloor. *A*, Alteration mineralogy of a stockwork zone exposed by faulting on the Galapagos Rift after Ridley and others (1994). *B*, Alteration mineralogy at the TAG deposit Honnorez and others (1998). *C*, Alteration zonation at Pacmanus, Ocean Drilling Program (ODP) Leg 193, Manus Basin, Papua New Guinea (PNG) after Binns and others (2007). *D*, Middle Valley alteration zonation after Goodfellow and Peter (1994). [Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Na, sodium; ab, albite; anh, anhydrite; chl, chlorite; ct, calcite; mu, muscovite; py, pyrite; qtz, quartz; ru, rutile; sm, smectite]

sediments, a 39-m interval of basaltic sills and sediment, and 29 m of basaltic flows. The entire sedimentary section beneath the deposit, including the feeder zone, is altered to chlorite and quartz (Lackschewitz and others, 2000), including layers of monomineralic chlorite. On the flanks of the deposit, less intense alteration produced dolomite, mixed-layer chlorite-smectite, corrensite, chlorite, and quartz. Teagle and Alt (2004) studied alteration in the deep basalt sills and flows and found quartz, chlorite, and titanite, with subsidiary epidote, Cu-Fe sulfides, and rare actinolite.

A broader, more distal picture of alteration in the oceanic crust emerges from studies of ODP Site 504, where repeated deepening of drill holes has now penetrated successively oxidized and weathered upper lavas, altered lower lavas, a transition zone that contains a sulfide stockwork, and more than 1 km of altered sheeted dikes (Alt and others, 1996). The lava section is 572 m thick with the upper half altered to iron oxides, carbonates, clays, and zeolites. The lower lava section is altered to chlorite and mixed-layer chlorite-illite, talc, zeolites, quartz, calcite, pyrite, and anhydrite. The transition zone and upper dikes were altered as upwelling hydrothermal fluids mixed with cooler seawater, producing heterogeneous alteration assemblages that include chlorite, actinolite, albite-oligoclase, and titanite and, in places, quartz-epidote-sulfide in discordant veins that record upflow zones. The lower dikes have an early, high-temperature (>400°C) alteration stage that produced hornblende and calcic plagioclase, consistent with reactions predicted from experimental studies (Seyfried and Shanks, 2004). Zones that contain these higher temperature alteration reactions are believed to represent the deep reaction zone for VMS producing systems, an interpretation confirmed by Cu, Zn, and S depletions in the altered rocks of the lower dikes (Alt and others, 1996).

## Alteration Zoning in Ancient Volcanogenic Massive Sulfide Deposits

Australian VMS deposits (Large, 1992), which are mostly bimodal-felsic types, have stringer zones that are dominated by chlorite-quartz associated with sulfides. Strong chlorite-sericite-quartz-pyrite alteration occurs in envelopes surrounding stringer zone mineralization. Less intense alteration, further from the deposits, is sericite-quartz-pyrite.

Ancient unmetamorphosed to weakly metamorphosed deposits (Cyprus, Kuroko, Noranda, Turkey) show spatial differences in Fe/(Fe+Mg) ratios of chlorite and related Fe-Mg phyllosilicates with distance from the sulfide ores. High Fe/(Fe+Mg) chlorite typically occurs in cores of feeder zones (Millenbach, Mathiati) and low Fe/(Fe+Mg) chlorite occurs along the margins (Lydon, 1996). These effects apparently are due to sealing of the inner parts of the feeder zone from seawater influx and alteration by the undiluted endmember hydrothermal fluid flow in the core of the feeder zone. The opposite pattern has been observed in a few deposits where presumably seawater was entrained into the feeder zone core (see Large,

1992; Gifkins and others, 2005). In metamorphosed deposits, primary Fe/(Fe+Mg) ratios in tourmaline are preserved, such as at Kidd Creek, where tourmalines in the core of feeder zone are Fe-rich whereas those along the margins are Mg-rich (Slack and Coad, 1989). Additionally, stratabound and stratiform chlorite-rich layers and lenses, which in places are nearly monomineralic chloritites, occur in the immediate footwall or hanging wall. Chlorite-rich layers, lenses, and veins likely form via seawater entrainment into ascending hydrothermal fluids, with seawater providing Mg for metasomatic processes.

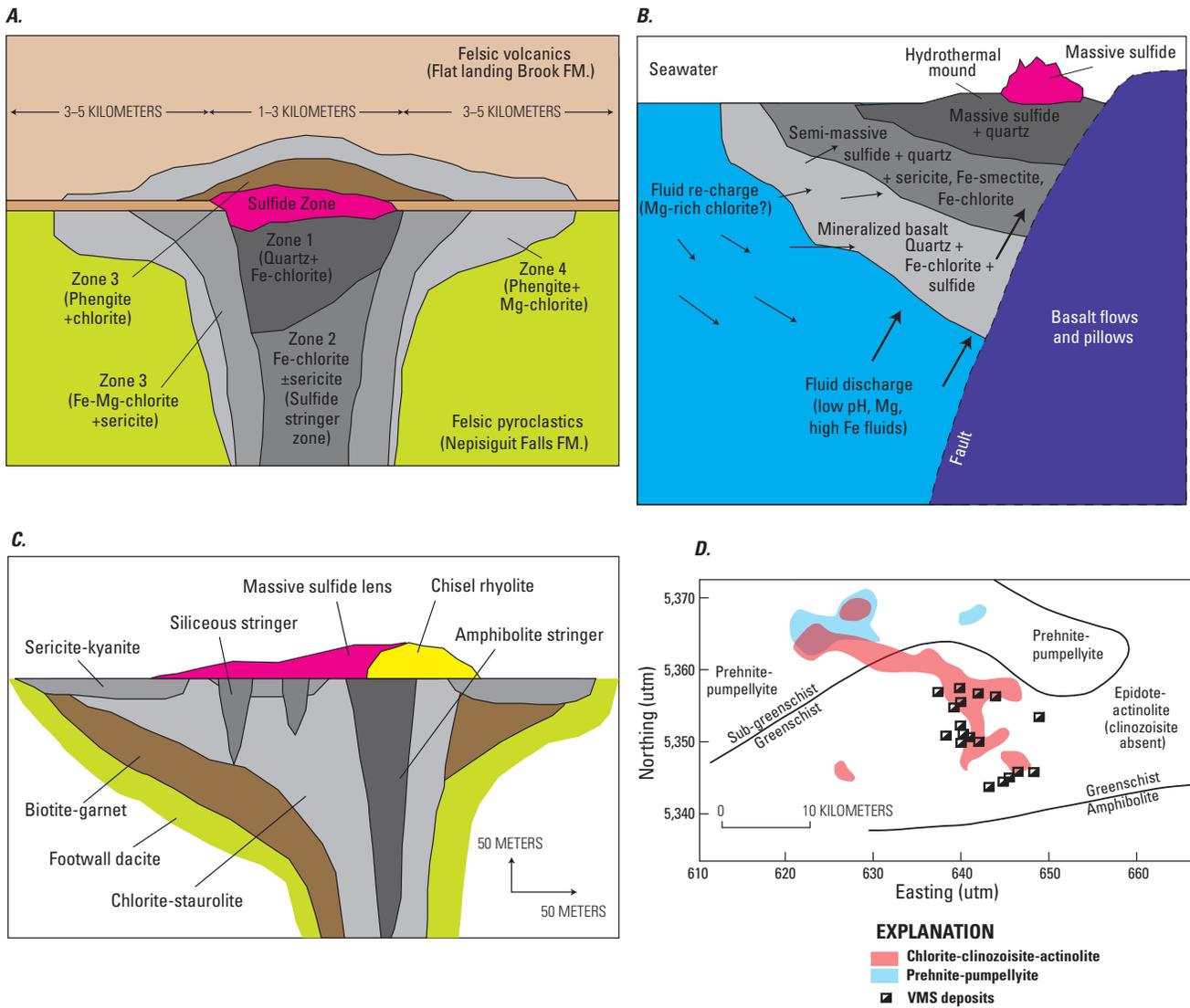
Representative examples of alteration zoning from several VMS deposit subtypes (fig. 11–2) include a siliciclastic-felsic type (Bathurst, New Brunswick), a mafic type (Turner-Albright, Josephine Ophiolite, Oreg.), and bimodal-mafic types at Chisel Lake, Manitoba, and bimodal-mafic deposits in the Noranda district, Quebec.

Alteration in the Bathurst district (fig. 11–2A) (Goodfellow, 2007) shows quartz and Fe-rich chlorite immediately underlying the massive sulfide and in the stockwork zone. Peripheral to that is a Mg-rich chlorite-sericite zone, which transitions outward to chlorite-phengite (silica-enriched sericite). Bathurst deposits also show phengite-chlorite alteration in the hanging wall above the massive sulfide horizon, which records ongoing hydrothermal activity after burial of the deposit.

Alteration in the mafic, ophiolitic Turner-Albright deposit (fig. 11–2B) (Zierenberg and others, 1988) shows an alteration pattern related to replacement mineralization in a porous and permeable hyaloclastite pile with general similarities to alteration at TAG and the Galapagos Rift (fig. 11–1A and B). Immediately beneath the massive sulfide deposit, quartz-sulfide alteration is prevalent as a result of massive replacement of basalt hyaloclastite. Beneath this are zones of quartz-sericite-smectite-chlorite and quartz-chlorite.

Deposits in metamorphosed terranes like the Chisel Lake deposit in the Snow Lake district, where alteration has undergone amphibolite-grade regional metamorphism (fig. 11–2C), show distinct assemblages related to premetamorphic alteration. In this deposit, the stringer zones are quartz- and amphibole-rich, and peripheral alteration consists of chlorite-stauroilite and biotite-garnet zones (Galley and others, 1993).

Semi-conformable alteration zones that occur in many VMS districts can be traced over many kilometers of strike length (fig. 11.–2D) (Galley, 1993; Hannington and others, 2003), and are clearly discordant to regional metamorphic isograds. Such conformable zones are probably related to premetamorphic, horizontal hydrothermal circulation driven by the heat of underlying sills or other intrusive bodies. One distinctive type of semi-conformable alteration comprises white mica+chloritoid±chlorite±carbonate assemblages in the stratigraphic footwall of deposits such as Mattabi in Ontario (Franklin and others, 1975) and those in the Delta district of northern Alaska (Dashevsky and others, 2003). This type of alteration reflects pervasive hydrothermal metasomatism of permeable felsic volcanic or volcanoclastic rocks involving alkali leaching, iron addition, and residual enrichment of



**Figure 11-2.** Representative examples of alteration zoning in volcanogenic massive sulfide deposits. *A*, Hydrothermal alteration in the Bathurst district after Goodfellow (2007). *B*, Alteration in the mafic, ophiolitic Turner-Albright, OR, deposit (Zierenberg and others, 1988) shows an alteration pattern related to replacement mineralization in a porous and permeable hyaloclastite pile with general similarities to alteration at TAG and the Galapagos Rift. *C*, Chisel Lake deposit in the Snow Lake district, Manitoba, where alteration has undergone amphibolite-grade regional metamorphism (Galley and others, 1993). *D*, Semi-conformable alteration zones (Hannington and others, 2003) that are clearly discordant to regional metamorphic isograds in the Blake River Group, Noranda volcanic complex, western Abitibi subprovince, Ontario. [Fe, iron; Mg, magnesium; Fm., formation]

alumina, followed by greenschist-grade regional metamorphism. At higher amphibolite metamorphic grade, mineral assemblages in these semi-conformable zones may contain abundant kyanite, sillimanite, or cordierite.

## Lateral and Vertical Dimensions

Dimensions of alteration zones are often difficult to determine because of lack of exposure and lack of drilling beyond the vicinity of VMS deposits. Most proximal alteration zones can be traced for approximately 2–3 times the horizontal dimension of the massive sulfide deposit and may extend to depths roughly 10 times the thickness of the deposit (figs. 6–1, 11–1, 11–2). Many deposits overlie semi-conformable alteration zones that can have a strike length of 5–50 km and thicknesses of 1–3 km, especially in caldera settings (Galley and others, 2007).

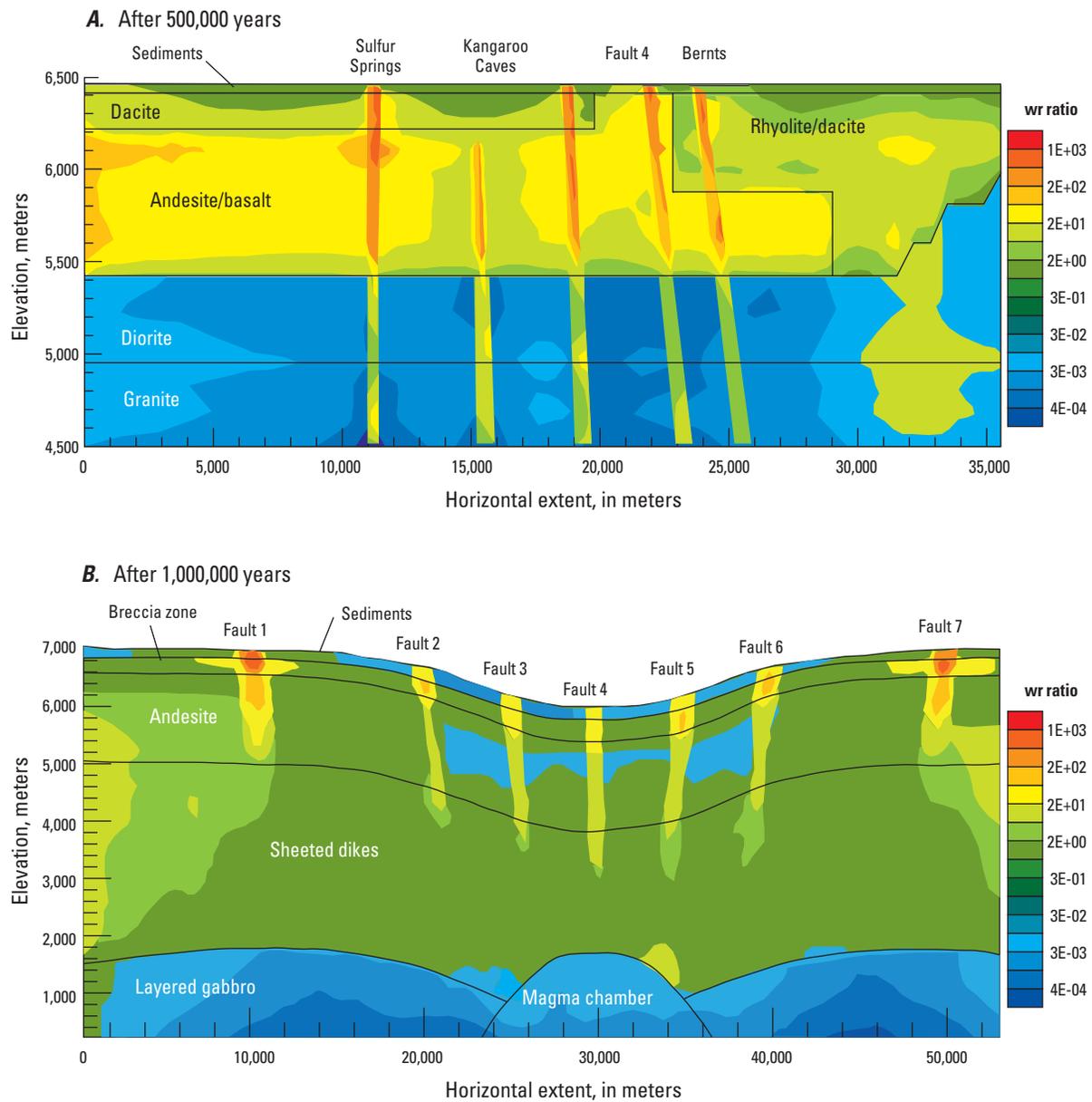
Fluid flow modeling has been used extensively to help constrain seafloor processes in modern and ancient massive sulfide deposits (Parmentier and Spooner, 1978; Cathles, 1983; Lowell and Rona, 1985; Schardt and Large, 2009). These models are limited by lack of information on crustal architecture, structures, permeability, magmatic heat supply, and fluid properties in the sub- and super-critical regions. However, the most recent models include many of these variables. Schardt and Large (2009) have attempted modeling with realistic permeability structures (fig. 11–3). Results indicate intense alteration along faults with dimensions up to a few hundred meters. In some cases, semi-conformable alteration is produced with dimensions of 500–700 m vertically and up to 30 km horizontally, but these dimensions are probably strongly affected by the dimensions of the model and the permeability structure within the volcanic sequence. Nevertheless, this fluid flow modeling approach has great potential for future understanding of alteration processes.

## Alteration Intensity

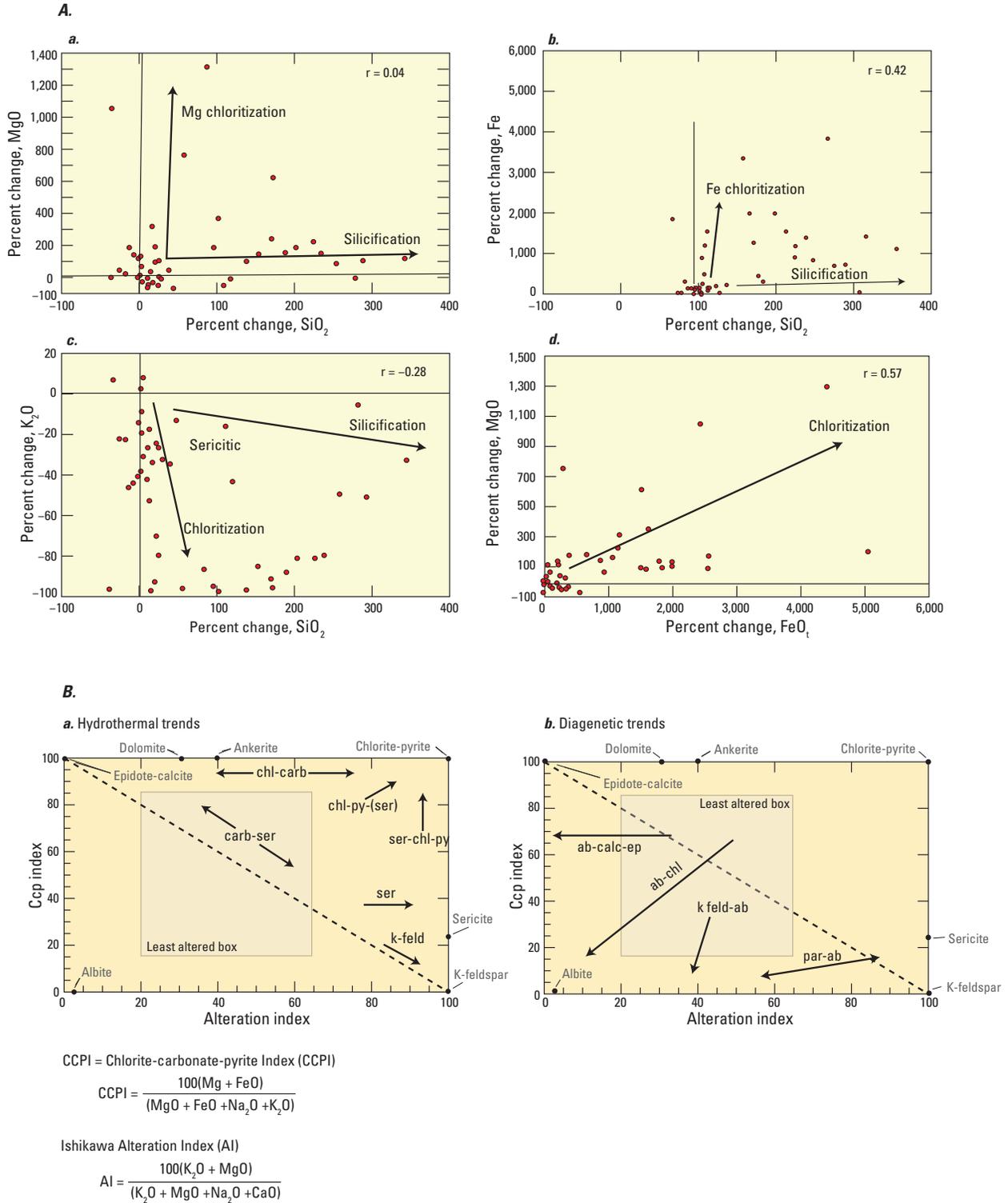
Alteration intensity is often described in the field using qualitative terminology such as weak-moderate-strong or incipient-patchy-pervasive, and these descriptions are critical to mapping and understanding alteration patterns. However, the recent literature abounds with quantitative tools for measuring and discriminating alteration intensity (Leitch and Lentz, 1994; Large and other, 2001b). These tools allow quantification of elemental gains and losses (and volume gain or loss) and characterization of specific types of alteration. The tools are increasingly important in exploration and, in ideal cases, may provide vectors to more intense alteration and mineralization. They also have great potential for use in mineral resource assessments; simple whole-rock geochemical data for altered rocks and representative fresh rocks are all that are needed for this type of analysis.

Gresens (1967) introduced mass balance approaches to metasomatic analyses, and Leitch and Lentz (1994) provided an update on effective application of the Gresens method, which essentially involves normalization relative to fresh unaltered rocks using immobile elements and calculation of volume changes during alteration using densities or compositional changes. Results of this approach for the Brunswick No. 12 deposit in the Bathurst district are shown in figure 11–4A. In this case, the percent change of major oxides clearly shows trends for silicification and for addition of hydrothermal sericite, Mg-chlorite, and Fe-chlorite. Changes in oxide content as large as 5,000 percent indicate that very intense metasomatism was involved in the alteration process. Numerous workers have applied these techniques to alteration studies in volcanogenic massive sulfide systems (Galley and others, 1993; Goodfellow and Peter, 1994; Barrett and MacLean, 1999; Gemmill and Fulton, 2001; Large and others, 2001a; Piercey, 2009).

Another approach is the alteration box plot of Large and others (2001b), which combines (1) the alteration index (AI) of Ishikawa defined as the ratio of  $K_2O + MgO$  to the sum of all alkaline and alkaline earth oxides versus (2) a new chlorite-carbonate-pyrite (CCP) index defined as the ratio of  $MgO + FeO$  to these oxides plus alkali oxides (fig. 11–4B). Combining these indices on a common plot yields clear identification of alteration processes that affect whole-rock composition (fig. 11–4B). This approach allows individual reactions to be identified and offers potential for discriminating burial diagenetic and hydrothermal processes, which may be essential in assessing mineral resource potential of a terrane.



**Figure 11-3.** Fluid flow modeling showing water/rock ratios during hydrothermal circulation (A) at the Panorama volcanogenic massive sulfide district and (B) beneath the seafloor at the Lau Basin hydrothermal system. Areas of high water-rock ratio are inferred to be intensely altered due to the high flux of reactant fluid. From Schardt and Large (2009). [wr, water/rock]



**Figure 11-4.** Geochemical techniques for quantifying hydrothermal alteration effects using (A) the Gresens mass balance approach and (B) the alteration box plot approach. Both approaches allow identification of alteration reactions and quantification of the amount of alteration. A, Percent change alteration plots for the Brunswick No. 12 deposit based on the Gresens approach and normalizing to  $Al_2O_3$  after Leitch and Lentz (1994). B, Alteration box plots after Large and others (2001). [Mg, magnesium; ab, albite; calc, calcite; carb, carbonate; chl, chlorite; ep, epidote; k-feld, potassium feldspar; par, paragonite; py, pyrite; ser, sericite; CCP, chlorite-carbonate-pyrite]

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