

# APPENDIX V



## Deposition of a high-sulfidation Au assemblage from a magmatic volatile phase, Volcán Popocatépetl, Mexico

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### Abstract

Volcán Popocatépetl (Popo) is a Quaternary stratovolcano located 70 km SE of Mexico City in the Trans-Mexican Volcanic Belt. The summit crater of Popo is the site of recent ash eruptions, degassing bursts, and dacite-dome growth. Fresh pumice samples collected on the flanks of Popo contain sparse, very fine-grained, base- and precious-metal phases that crystallized from magmatic volatiles trapped in vesicles. The assemblages consist of pyrite, sphalerite, chalcocopyrite, tennantite, galena, enargite, magnetite, chromite, and barite; some samples also contain calaverite, stannite, AuCu telluride, Ag sulfide, AgCu sulfide, AgFe sulfide, Ag bromide, Ag chloride, Bi chloride, halite, kaolinite, and alunite. These assemblages are similar to those found in high-sulfidation epithermal Au deposits, and provide evidence consistent with a direct magmatic source for metals in those deposits. Bulk-sample concentrations of base and precious metals are not anomalously high and can be accounted for mainly by the presence of ore minerals in vesicles; this suggests that a high proportion of the metal content of the original magma was partitioned into a volatile phase which subsequently was trapped and condensed.

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**Keywords:** magma; vesicles; pumice; sulfides; sulfosalts; degassing; gold; silver; tellurium

### 1. Introduction

The close spatial relationship and similarities in alteration type between porphyry Cu and high-sulfidation epithermal deposits have suggested a genetic connection between the two styles of mineralization (Sillitoe, 1983, 1989; Arribas et al., 1995b). It is widely accepted that magmatic fluids are the sources of ore metals in porphyry environments, and there is isotopic evidence for ascending magmatic volatiles mixing with meteoric waters to form altering fluids in high-sulfidation epithermal systems (e.g., Giggenbach, 1992; Rye, 1993; Arribas

et al., 1995a). However, the evidence for a magmatic source of metals in epithermal systems and the mechanism of their transport to higher levels remain subjects of debate (Hedenquist and Lowenstern, 1994; Williams-Jones et al., 2005).

Candela (1989) summarized some of the processes involved in the separation of a magmatic volatile phase (MVP) during final emplacement of a hydrous felsic magma. During advanced crystallization of a silicic melt, volatile species such as H<sub>2</sub>O, CO<sub>2</sub>, and S gases dissolved in the melt reach saturation, and exsolve to form an MVP. Incompatible elements can be strongly partitioned into the MVP, although the availability of base and precious metals for partitioning into the volatile phase depends on the timing of vapor-phase segregation relative to the growth of phenocrysts or separation of immiscible melts that may sequester metals. The MVP is a supercritical fluid which, upon cooling, can separate into a saline aqueous fluid and a vapor. Metals can be variably partitioned between these two phases,

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## EVIDENCE FOR OPEN-SYSTEM BEHAVIOR IN IMMISCIBLE Fe-S-O LIQUIDS IN SILICATE MAGMAS: IMPLICATIONS FOR CONTRIBUTIONS OF METALS AND SULFUR TO ORE-FORMING FLUIDS

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### ABSTRACT

Magmatic sulfides are generally accepted as forming by segregation of an immiscible sulfide liquid from a host silicate melt. Immiscible sulfides have been observed in many types of igneous rocks; however, some types of plutonic and volcanic rocks lack sulfides. We have examined a suite of samples from Mount Pinatubo (Philippines), Volcán Popocatepetl (Mexico), Satsuma-Iwojima (Japan) and Mount St. Helens, Bingham Canyon, Tintic District, and Clear Lake (U.S.A.). The samples reflect a range of crystallization histories and compositions; they range from rhyolite to basalt to trachyandesite, with  $f(\text{O}_2)$  at the time of eruption ranging from below the fayalite – magnetite + quartz (FMQ) buffer to well above the nickel – nickel oxide (NNO) buffer. Textural and chemical evidence from our suite of samples indicate that sulfides initially were present, but were modified prior to complete cooling of the parent melt, giving rise to Fe-oxide globules. The globules formed through: (1) segregation of an immiscible Fe-S-O melt, and possibly, further separation of immiscible Fe-S and Fe-O liquids, and (2) undersaturation with respect to sulfide, causing removal of S from the immiscible sulfide melt. Sulfide undersaturation may have been caused by magma degassing (passively or during eruption), or magma mixing. The recognition of modified magmatic sulfides is important because, with extensive degassing, base and precious metals (e.g., Cu, Au) could be stripped from a melt by a S-rich magmatic volatile phase and entrained into a magmatic-hydrothermal fluid, ultimately giving rise to porphyry-type or related mineralization. For a melt containing 0.01 modal % magmatic sulfides, efficient degassing of only 10 km<sup>3</sup> of magma could yield enough Cu to form a giant deposit.

**Keywords:** magmatic sulfides, immiscible Fe-S-O melt, degassing, magma mixing, Pinatubo, Popocatepetl, Mount St. Helens, Bingham, Tintic, Satsuma-Iwojima, Clear Lake, porphyry deposit.

### SOMMAIRE

On accepte en général que les sulfures magmatiques se sont formés par ségrégation d'un liquide sulfuré immiscible à partir d'un magma hôte silicaté. La présence de sulfures immiscibles a été signalée dans plusieurs types de roches ignées; toutefois, il faut aussi dire que certains types de roches plutoniques et volcaniques sont dépourvus de sulfures. Nous avons examiné une suite d'échantillons provenant du mont Pinatubo (Philippines), du volcan Popocatepetl (Mexique), Satsuma-Iwojima (Japon), du mont St. Helens et des localités Bingham Canyon, Tintic District, et Clear Lake (Etats-Unis). Les échantillons font preuve d'une variété de modes de cristallisation et de compositions; ils représentent le spectre de composition allant de rhyolite à basalte à trachyandésite, la fugacité d'oxygène  $f(\text{O}_2)$  lors de l'éruption allant de conditions inférieures au tampon fayalite – magnétite + quartz (FMQ) dans certains cas à des conditions au delà du tampon nickel – oxyde de nickel (NNO). D'après les critères texturaux et géochimiques, les sulfures étaient présents à l'origine dans notre suite d'échantillons, mais ils ont été modifiés avant le refroidissement final du liquide silicaté parental, ce qui est responsable de la formation de globules d'oxyde de fer. Ces globules se sont formés (1) par ségrégation d'un liquide Fe-S-O immiscible, et peut-être, séparation éventuelle en liquides Fe-S et Fe-O immiscibles, ou (2) sous-saturation par rapport au sulfure, ce qui mena à la perte de soufre du liquide immiscible sulfuré. Cette

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RESEARCH ARTICLE

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## The crater lake and hydrothermal system of Mount Pinatubo, Philippines: evolution in the decade after eruption

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**Abstract** The June 1991 eruption of Mount Pinatubo, Philippines breached a significant, pre-eruptive magmatic-hydrothermal system consisting of a hot ( $>300^{\circ}\text{C}$ ) core at two-phase conditions and surrounding, cooler ( $<260^{\circ}\text{C}$ ) liquid outflows to the N and S. The eruption created a large, closed crater that accumulated hydrothermal upwellings, near-surface aquifer and meteoric inflows. A shallow lake formed by early September 1991, and showed a long-term increase in level of  $\sim 1$  m/month until an artificial drainage was created in September 2001. Comparison of the temporal trends in lake chemistry to pre- and post-eruptive springs distinguishes processes important in lake evolution. The lake was initially near-neutral pH and dominated by meteoric influx and  $\text{Cl-SO}_4$  and  $\text{Cl-HCO}_3$  hydrothermal waters, with peaks in  $\text{SO}_4$  and Ca concentrations resulting from leaching of anhydrite and aerosol-laden tephra. Magmatic discharge,

acidity ( $\text{pH}\sim 2$ ) and rock dissolution peaked in late 1992, during and immediately after eruption of a lava dome on the crater floor. Since cessation of dome growth, trends in lake pH (increase from 3 to 5.5), temperature (decline from  $40$  to  $26^{\circ}\text{C}$ ), and chemical and isotopic composition indicate that magmatic degassing and rock dissolution have declined significantly relative to the input of meteoric water and immature hydrothermal brine. Higher concentrations of Cl, Na, K, Li and B, and lower concentrations of Mg, Ca, Fe,  $\text{SO}_4$  and F up to 1999 highlight the importance of a dilute hydrothermal contribution, as do stable-isotope and tritium compositions of the various fluids. However, samples taken since that time indicate further dilution and steeper trends of increasing pH and declining temperature. Present gas and brine compositions from crater fumaroles and hot springs indicate boiling of an immature  $\text{Cl-SO}_4$  geothermal fluid of near-neutral pH at approximately  $200^{\circ}\text{C}$ , rather than direct discharge from magma. It appears that remnants of the pre-eruptive hydrothermal system invaded the magma conduit shortly after the end of dome emplacement, blocking the direct degassing path. This, along with the large catchment area ( $\sim 5\text{ km}^2$ ) and the high precipitation rate of the area, led to a rapid transition from a small and hot acid lake to a large lake with near-ambient temperature and pH. This behavior contrasts with that of peak-activity lakes that have more sustained volcanic gas influx (e.g., Kawah Ijen, Indonesia; Poas and Rincón de la Vieja, Costa Rica).

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**Keywords** Mount Pinatubo · Volcanic crater lake · Lake formation · Fluid chemistry · Magmatic-hydrothermal system · Helium isotopes · Stable isotopes · Tritium

### Introduction

Lakes commonly form in closed volcanic craters and calderas through accumulation of precipitation, ground-water and magmatic-hydrothermal discharges. Such lakes condense ascending magmatic vapor and hydrothermal



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## Chapter 2

### Regional Metamorphic Remobilization: Upgrading and Formation of Ore Deposits

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#### Abstract

Metamorphic remobilization involves the translocation, during deformation and metamorphism, of preexisting, massive, semimassive, or disseminated mineralization by solid-state mechanical transfer, liquid-state chemical transfer, or mixed-state transfer. Mixed-state processes, in which deformation plays a critical role, have dominated in nature. The terminology and concepts involved in remobilization are discussed; internal and external processes, extent of remobilization, parent-daughter relationships, and upgrading of ore are particularly emphasized.

The series of textural and mineralogical changes brought about by prograde metamorphism generally have little impact on the overall grades of the major, minor, and trace elements present. However, effective upgrading by grain size coarsening and formation of discrete trace element (e.g., precious element) minerals enables more efficient recovery. Some prograde changes can be reversed during retrogression.

Consideration is given to the probable extent of selective external remobilization of components from sulfide orebodies. Large-scale selective removal of components from massive ore is difficult to substantiate on both observational and theoretical bases. It is nevertheless concluded that such remobilization cannot entirely be rejected.

Transfer processes in regional metamorphic remobilization include cataclasis and granular flow, intracrystalline plasticity or dislocation flow, and dry- and wet-state diffusion, with the latter commonly being grouped with advective transfer. Because several processes may be rate competing in a single phase, although the dominant mechanism may differ between phases, consideration is facilitated by addressing solid-state remobilization before conjointly dealing with mixed and liquid state processes.

Intergranular and intragranular solid-state transfer is fundamental to dry-state ductile deformation, and of great importance for the degree of internal remobilization. Dislocation flow has been invoked to explain healing of fractures in high competence sulfides by low competence species, but fluid facilitation should not be discounted. Internal solid-state remobilization can form ore shoots by hinge zone thickening and elongation processes, although fluid-assisted diffusive and advective mass transfer probably contribute significantly to these cases. External solid-state remobilization has been invoked to explain piercement cusps and veins, as well as discordant, shear zone-hosted bodies of enriched mineralization, yet a degree of fluid involvement is usually envisaged. In effect, there are few, if any, undoubted examples of solid-state external remobilization.

The bulk of extensive internal and external remobilization involves mixed- or liquid-state transfer, the liquid phase having a range of possible origins. Pertinent mass transfer paths include diffusion around grain boundaries through a static film, flow around grain boundaries and through dynamic microfracture networks, and channelized flow through macrofracture systems, now commonly seen as vein arrays related to ductile and brittle shear zones. A substantial extent of remobilization will only result from the advecting processes. Liquid-state involvement in mixed-state transfer ranges from negligible or subordinate to totally dominating, before passing into true liquid-state transfer. The spectrum of mixed- and liquid-state processes includes fluid-controlled cataclasis, fluid-induced dislocation flow, fluid-facilitated shear zone transfer, fluid-assisted diffusion, fluid-dominated transfer, and advective transfer; each is assessed.

Magmatic transfer in the remobilization of sulfide species potentially results from production of sulfide melts during high-grade metamorphism, dissolution of ore minerals by a migrating silicate melt, and

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Chapter 8

## Ion-Microprobe Quantification of Precious Metals in Sulfide Minerals

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### General Principles

SIMS (secondary-ion mass spectrometry) is an analytical technique for the surface, near-surface, and bulk characterization of solids. The technique uses a primary beam of ions to sputter a sample surface, producing a secondary beam of ionized particles (secondary ions) that are passed through a mass spectrometer. Acquired data may be presented as mass spectra, depth profiles showing element concentrations or isotope ratios, and ion images. SIMS has a number of advantages over electron-beam and X-ray analytical techniques. Secondary-ion intensities can be measured over a dynamic range of nine orders of magnitude (vs. two orders of magnitude for AES and XPS). All elements may be detected, and their isotopes distinguished. Detection limits range from ppm to ppb. Depth profiling and ion imaging are possible, with excellent depth and

lateral resolution. Because of the low detection limits that may be obtained with SIMS, this technique is invaluable for the quantification of precious metals, which commonly occur in very low concentrations. In addition, the depth-profiling and imaging capabilities of SIMS reveal whether metals are present as submicroscopic inclusions or are dispersed throughout the matrix; this information is important for maximizing the efficiency of mineral processing.

Figure 1 shows a schematic of the ion optical system for the Cameca ims 4f ion microprobe. Primary ions are produced in a duoplasmatron or cesium source, then extracted, mass filtered and accelerated by a high voltage (10–30 kV). A series of electrostatic lenses and apertures in the primary column focuses the mono-ionic beam onto the sample. The primary beam impacts the sample and sputters secondary ions (both single ions and “molecular” ions) as well as neutral atoms, X-rays, and electrons. The

### The ion optical system

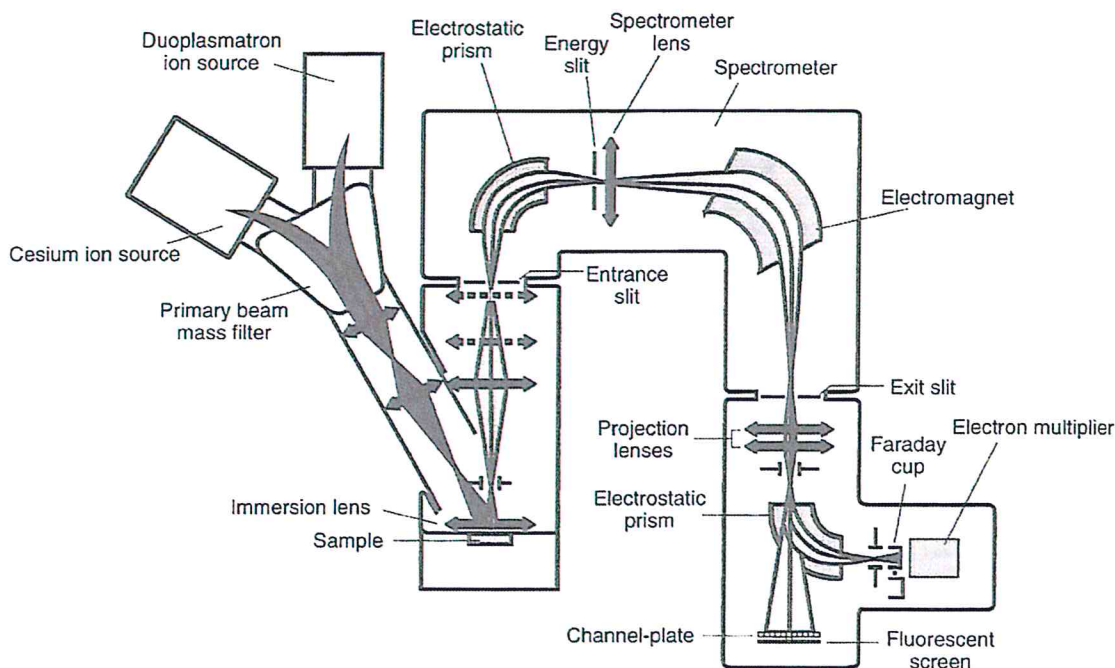


FIG. 1. Schematic of the ion optical system for the Cameca ims 4f ion microprobe. The black double-pointed arrows indicate the positions of various lenses in the primary and secondary columns.



# An overview of trace metals in the environment, from mobilization to remediation

Adrienne C. L. Larocque · Patricia E. Rasmussen

## Introduction

This special issue of *Environmental Geology* arose from a symposium on *Trace Metals in the Environment* held at the Geological Association of Canada - Mineralogical Association of Canada (GAC-MAC) Joint Annual Meeting in Winnipeg, Manitoba in 1996. Most of the papers in this special issue are based on presentations made at the symposium. The ultimate goal of the symposium was to bring together workers doing research in diverse fields, all involving metal speciation and transport. More than any other area of scientific endeavor, environmental research demands a multidisciplinary approach. We have much to learn from each other, and together we can move toward a better understanding of metal cycling in the environment.

## An environmental model

Our environment, the place where we live, is the planet Earth. The Earth is made up of three reservoirs: the solid Earth or *geosphere*, the liquid layer or *hydrosphere*, and the gaseous envelope or *atmosphere* (Fig. 1). Living organisms (the *biosphere*) inhabit the Earth environment, interacting with its component parts. There is a continuous exchange of matter and energy among the geosphere, hydrosphere and atmosphere. The nature of these reservoirs and the processes involved in transferring energy and matter between them combine to create an environment that is capable of sustaining life in its many forms, a situation unique in our solar system. Metals in the environment may be present in the solid, liquid or gaseous state. They may be present as individual elements, and as organic and inorganic compounds. The movement of metals between environmental reservoirs may or may not involve changes of state.

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The geosphere is the original source of all metals (except those that enter the atmosphere from space in the form of meteorites and cosmic dust). Within the geosphere, metals may be present in minerals, glasses, and melts. In the hydrosphere, metals occur as dissolved ions and complexes, colloids, and suspended solids. In the atmosphere, metals may be present as gaseous elements and compounds and as particulates and aerosols. Gaseous and particulate metals may be inhaled and solid and liquid (aqueous-phase) metals may be ingested or absorbed, thereby entering the biosphere. In addition to being the original source of all terrestrial metals, the geosphere may represent a sink for metals. The atmosphere and hydrosphere also constitute sinks for metals; however, from a geological perspective, they are more likely to be considered agents of transport. Whether we define an environmental reservoir as a sink or as a medium for the movement of metals from one site to another depends on the linear and temporal scales of observation. For example, the oceans are a vast reservoir for a variety of chemical elements. However, they also are a conduit for elements derived from weathering of rocks to return to the geosphere through sedimentation. Finally, a reservoir may act as a catalyst for changes of state of metals and metal compounds, without actually having incorporated those metals, as in the case of some biologically mediated reactions.

Figure 1 shows a comprehensive model for metal transport. It takes into account all reservoirs, whether they represent sources, sinks, or agents of transport. This model illustrates the "natural" interactions between environmental reservoirs. Figure 2 shows how the segment of the biosphere occupied by humans interacts with the environment. Figure 2 includes mechanisms and processes similar to those illustrated in Fig. 1. For example, dumping of wastes into lakes and rivers and production of emissions from smelting of ores may be viewed as a form of excretion by society as a whole rather than by an individual cell or organism. Most efforts to remediate metal contamination involve fixing metals in a solid form and returning them to their original source - the geosphere (Fig. 2).

The presentations in the symposium at GAC-MAC and the papers in this special issue illustrate different parts of the model. Some workers focussed on characterization of materials within individual reservoirs, whereas others documented experiments designed to understand mecha-



# Metal-residence sites in lavas and tuffs from Volcán Popocatepetl, Mexico: implications for metal mobility in the environment

Adrienne C. L. Larocque · James A. Stimac · Claus Siebe

**Abstract** Volcan Popocatepetl is a Quaternary stratovolcano located 60 km southeast of Mexico City. The summit crater is the site of recent ash eruptions, excess degassing, and dacite dome growth. The modern cone comprises mainly pyroclastic flow deposits, airfall tephra, debris flows, and reworked deposits of andesitic composition; it is flanked by more mafic monogenetic vents. In least-degassed fallout tuffs and mafic scoria, transition metals are concentrated in phases formed before eruption, during eruption, and after eruption. Pre-eruptive minerals occur in both lavas and tephra, and include oxides and sulfides in glass and phenocrysts. The magmatic oxides consist of magnetite, ilmenite, and chromite; the sulfides consist of both  $(\text{Fe,Ni})_{1-x}\text{S}$  (MSS) and Cu-Fe sulfide (ISS). Syn- and post-eruptive phases occur in vesicles in both lavas and tephra, and on surfaces of ash and along fractures. The mineral assemblages in lavas include Cu-Fe sulfide and Fe-Ti oxide in vesicles, and Fe sulfide and Cu-Fe sulfide in segregation vesicles. Assemblages in vesicles in scoria include Fe-Ti oxide and rare Fe-Cu-Sn sulfide. Vesicle fillings of Fe-Ti oxide, Ni-rich chromite, Fe sulfide, Cu sulfide, and barite are common to two pumice samples. The most coarse-grained of the vesicle fillings are Cu-Fe sulfide and Cu sulfide, which are as large as 50  $\mu$  in diameter. The youngest Plinian pumice also contains Zn(Fe) sulfide, as well as rare Ag-Cu sulfide, Ag-Fe sulfide, Ag bromide, Ag chloride, and Au-Cu telluride. The assemblage is similar to

those typically observed in high-sulfidation epithermal mineralization. The fine-grained nature and abundance of syn- and/or post-eruptive phases in porous rocks makes metals susceptible to mobilization by percolating fluids. The abundance of metal compounds in vesicles indicates that volatile exsolution prior to and/or during eruption played an important role in releasing metals to the atmosphere.

**Key words** Metals · Sulfides · Vapor-phase crystallization · Cu · Arc volcano · Volcanic emissions

## Introduction

Evidence from volcanic plumes and fumarolic sublimates indicates that some elements are partitioned into the vapor phase during eruption and shallow degassing of magmas (Stoiber and Rose 1974; Bernard and others 1990; Meeker and others 1991; Symonds and Reed 1993; Hinkley and others 1994). From an environmental perspective, understanding the nature and magnitude of element partitioning is important because: (1) toxic metals are among those elements that are fractionated into the vapor phase (Symonds and others 1987; Papike and others 1991; Goff and others 1994); (2) large volumes of gas (and thus, large amounts of volatile metals) enter the atmosphere during eruption and passive degassing of volcanoes (summarized by Stimac 1996); and (3) volatile metals commonly are deposited as micron-scale coatings in porous tuffs, and may be mobilized by percolating groundwater (Stimac and others 1996). The purpose of this paper is to document residence sites of transition metals in lavas and tuffs from Volcán Popocatepetl in Mexico, and to relate metal mobility and siting to magmatic and volcanic processes.

Transition metals in volcanic rocks may be hosted by pre-eruptive, syneruptive, or post-eruptive phases. Pre-eruptive minerals form during fractional crystallization of parental magma, and occur as phenocrysts, microphenocrysts, and inclusions in phenocrysts. Segregation of immiscible Fe-S(-O) melts also gives rise to pre-eruptive

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## Redistribution of Pb and other volatile trace metals during eruption, devitrification, and vapor-phase crystallization of the Bandelier Tuff, New Mexico

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## THE OCCURRENCE OF GOLD IN SULFIDE DEPOSITS OF THE TAG HYDROTHERMAL FIELD, MID-ATLANTIC RIDGE\*

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### ABSTRACT

Sulfide deposits in the TAG Hydrothermal Field include both active and relict hydrothermal mounds, with high-temperature black smokers, lower-temperature white smoker chimneys, and coarse recrystallized massive sulfides. On the active TAG mound, black smoker chimneys consist mainly of pyrite-chalcopyrite assemblages (up to 24 wt.% Cu), with concentrations of gold from 0.03 to 1.7 ppm Au. Zn-rich sulfides from the mound are commonly gold-rich, with an average of 9.5 ppm Au and a median value of 6.0 ppm Au ( $n = 15$ ). White smokers from a low-temperature vent complex on the mound have gold contents of up to 42 ppm Au. In the white smokers, gold is present as submicroscopic particles or as "invisible" gold within fine-grained dendritic sphalerite that comprises the bulk of the chimneys. The significant enrichment of gold within the lower-temperature white smoker complex and the effective separation of Zn and Cu in hydrothermal precipitates at the surface of the mound are interpreted to reflect a strong thermal gradient within the central zone of upflow. Massive, Cu-Fe-Zn sulfides from a nearby relict sulfide mound, the MIR Mound, also are gold-rich. Concentrations of gold in the MIR sulfides reach 15.5 ppm Au, with an average of 7.6 ppm and a median value of 7.7 ppm ( $n = 13$ ). These samples are distinctly coarse-grained and show evidence of extensive hydrothermal recrystallization and replacement, as well as of overprinting by multiple hydrothermal events. Native gold in these samples occurs mainly as free grains up to 4  $\mu\text{m}$  in diameter, occupying open spaces in the massive sulfides, in late microfractures, and along grain boundaries between coarse recrystallized sulfides. Ion-microprobe analyses of pyrite and chalcopyrite indicate background concentrations of less than 2 ppm Au as invisible gold in the coarse-grained sulfides. The most abundant gold occurs in a late-stage, sphalerite-rich vein that cuts earlier massive pyrite; similar veins may have been feeders for gold-rich white smokers once present at the surface of the mound (*i.e.*, similar to those on the active TAG Mound). A history of high-temperature venting in the TAG Hydrothermal Field, spanning more than 50,000 years, has resulted in extensive hydrothermal reworking of the sulfide deposits. This process is considered to be important for the remobilization and local reconcentration of early-formed gold and may have been responsible for the formation of relatively coarse-grained, high-purity native gold in recrystallized massive sulfides from the MIR Mound.

**Keywords:** native gold, seafloor sulfides, Mid-Atlantic Ridge, TAG Hydrothermal Field, black smokers, white smokers, hydrothermal reworking.

### SOMMAIRE

Les gisements de sulfures du champ d'activité hydrothermale de TAG, sur la crête médio-atlantique, comprennent à la fois des amoncellements hydrothermaux actifs et éteints, des fumeurs noirs actifs à température élevée, des fumeurs blancs actifs à plus faible température, et des amas de sulfures massifs recristallisés, à grains grossiers. A cet endroit, les cheminées associées aux fumeurs noirs sont faites d'assemblages à pyrite + chalcopyrite (avec jusqu'à 24% de Cu en poids) ayant des teneurs en or

\* Geological Survey of Canada contribution number 68294.



## Effects of greenschist-facies metamorphism and related deformation on the Mobrun massive sulfide deposit, Québec, Canada

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**Abstract.** The Mobrun Zn-Cu-Ag-Au deposit in the Noranda mining camp is hosted by Archean mafic and felsic submarine volcanic rocks. The deposit comprises three massive sulfide complexes: the Main and Satellite Lenses near surface, and the 1100 orebody at depth. The rocks have been subjected to lower greenschist-facies metamorphism and related deformation, which resulted in changes in ore textures, development of shear zones and veins systems, remobilization of gold, and formation of a new mineral (electrum) within the orebodies. Both mechanical and chemical processes operated to produce secondary textures and structures resulting from brittle deformation, ductile deformation, and annealing. The specific deformation mechanisms include brittle failure and cataclastic flow, dislocation glide, dislocation creep and solution-precipitation creep. The Main and Satellite Lenses are characterized by excellent preservation of primary sulfides deposited from and reworked by synvolcanic hydrothermal fluids. These orebodies were affected to a limited degree by mechanical processes of deformation. In contrast, the 1100 orebody is characterized by a higher degree of development of textures and structures related to metamorphism and deformation, especially those formed by chemical processes. The differences may be due to the greater depth of the 1100 orebody relative to the other lenses, as regional metamorphic isograds are subhorizontal, and more extensive interaction between metamorphic fluids and the 1100 Lens.

Deformation experiments on natural polycrystalline sulfides have provided information on their mechanisms of deformation. Under greenschist-facies metamorphic conditions, pyrite deforms exclusively by cataclasis (Atkinson 1975; Cox et al. 1981). In contrast, chalcopyrite and

sphalerite deform ductilely, by intragranular (dislocation) sliding and deformation twinning (Clark and Kelly 1973; Kelly and Clark 1975; Roscoe 1975). Pyrrhotite, which undergoes brittle deformation at low temperature and pressure, deforms ductilely by twin-gliding at temperatures above 250°C (Clark and Kelly 1973). Interpretation of deformation textures may be made difficult by the fact that evidence of ductile deformation in sulfides may be obliterated by subsequent static (postdeformational) recrystallization or thermal annealing. This is especially common in pyrrhotite.

Examining the effects of deformation on monomineralic sulfide aggregates is useful, as it provides information about the relative importance of diffusion, slip, and intergranular deformation (Poirier 1985). However, the behaviour of individual sulfide minerals during metamorphism and related deformation of massive sulfide deposits may vary greatly, depending on temperature, strain rate, confining pressure, fluid pressure, differential stress, permeability within the zone of deformation, and the nature of adjacent or matrix-forming sulfides (Ashby and Verrall 1973; Kelly and Clark 1975; Knipe 1989; Cook et al. 1993; Duckworth and Rickard 1993). Cox (1987) subdivided deformation mechanisms in sulfide minerals into the following categories: 1) brittle failure and cataclastic flow; 2) low-temperature plasticity (dislocation glide and mechanical twinning); 3) dislocation creep; 4) solution-precipitation creep; 5) solid-state diffusion creep; and 6) grain-boundary sliding. The effects of metamorphism and deformation on massive sulfide deposits have been described by many authors (Vokes 1969; Mookherjee 1976; McClay 1991; Craig and Vokes 1992, 1993; Vokes and Craig 1993, among others).

The general effects of metamorphism and deformation on rocks comprise chemical/mineralogical changes, textural changes, and structural changes. In their study of sulfide deposits in the Appalachian – Caledonian Orogen, Craig and Vokes (1992) observed that metamorphism ranging from greenschist- to amphibolite-facies had little effect in altering the mineralogy; however, metamorphism had a significant effect on ore textures and the distribution of minor elements among co-existing minerals. Similarly,

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# ION-MICROPROBE ANALYSIS OF PYRITE, CHALCOPYRITE AND PYRRHOTITE FROM THE MOBRUN VMS DEPOSIT IN NORTHWESTERN QUEBEC: EVIDENCE FOR METAMORPHIC REMOBILIZATION OF GOLD

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## ABSTRACT

The Mobrun Zn-Cu-Ag-Au deposit, located in the Noranda District, in the Quebec segment of the Abitibi Greenstone Belt, is hosted mainly by felsic volcanic rocks of the Archean Blake River Group. Primary facies of mineralization in the Mobrun orebodies resulted from deposition and reworking of sulfides by synvolcanic hydrothermal fluids. Secondary facies of mineralization resulted from greenschist-grade metamorphism and related deformation, and locally overprinted the primary facies. The "invisible" (refractory) gold contents of pyrite, chalcopyrite and pyrrhotite in various facies were determined using a Cameca IMS-4f ion microprobe. Samples were sputtered with a Cs<sup>+</sup> primary beam, and negative secondary ions were measured. External standards of sulfides were implanted with <sup>197</sup>Au. Mass interferences were eliminated by operating in high-mass-resolution mode (M/ΔM in the range 2400 to 3900), giving rise to minimum limits of detections of 50 ppbw. Primary pyrite contains up to 10 ppmw gold, present as submicrometric inclusions of metallic gold, as well as very fine colloid-size or structurally bound gold. Concentrations of gold in associated secondary (recrystallized) pyrite range from 1 to 67% of the concentrations in primary pyrite. The results indicate that syngenetic gold is present in the Mobrun orebodies, and that metamorphic recrystallization resulted in its release from pyrite. The remobilized gold was deposited in tectonic veins as easily recoverable electrum and as "invisible" gold in secondary chalcopyrite. The partitioning of gold among various phases in secondary veins may have been influenced by the interaction between the remobilizing fluid and the assemblages of primary ore minerals.

**Keywords:** "invisible" gold, refractory gold, ion microprobe, SIMS, pyrite, chalcopyrite, pyrrhotite, electrum, remobilization, metamorphic recrystallization, volcanogenic massive sulfide, Mobrun, Noranda, Quebec.

## SOMMAIRE

Le gisement à Zn-Cu-Ag-Au de Mobrun, situé dans le district de Noranda, dans le secteur québécois de la ceinture de roches vertes de l'Abitibi, est encaissé dans une suite de roches volcaniques, surtout felsiques, du Groupe de Blake River, d'âge archéen. Les faciès primaires de minéralisation dans les gîtes de sulfures massifs se sont formés par déposition et par modification des sulfures par des fluides hydrothermaux synvolcaniques. Les faciès secondaires de minéralisation se sont formés par métamorphisme dans les faciès schistes verts et par déformation contemporaine, et localement ont obité les faciès primaires. Les teneurs en or "invisible" (réfractaire) de la pyrite, la chalcopyrite et la pyrrhotite dans plusieurs faciès de minéralisation ont été déterminées par microsonde ionique Cameca IMS-4f. Les échantillons ont été bombardés avec un faisceau d'ions primaires de Cs<sup>+</sup>, et les ions négatifs secondaires émis ont été mesurés. Les étalons externes de sulfures ont été implantés avec l'isotope <sup>197</sup>Au. On a pu éliminer les interférences de masse par opération dans le mode de haute résolution de masses (M/ΔM de 2400 à 3900), ce qui a permis un seuil de détection minimum de 50 ppb (poids). La pyrite primaire contient jusqu'à 10 ppm d'or, soit incorporé dans la structure, soit en inclusions submicrométriques ou encore de taille colloïdale. La pyrite secondaire (recrystallisée) contient entre 1 et 67% de la teneur en or de la pyrite primaire. Les résultats indiquent que l'or syngénétique est présent dans les gîtes de Mobrun, et que la recrystallisation métamorphique a libéré l'or de la pyrite, et l'a déposé dans les veines d'origine tectonique sous forme d'électrum, facilement recouvrable, et d'or "invisible" dans la chalcopyrite secondaire. La répartition de l'or parmi les divers minéraux des veines secondaires dépendrait possiblement de l'interaction de la phase fluide et l'assemblage de minéraux primaires.

**Mots-clés:** or "invisible", or réfractaire, microsonde ionique, spectrométrie de masse des ions secondaires, pyrite, chalcopyrite, pyrrhotite, électrum, remobilisation, recrystallisation métamorphique, sulfures massifs volcanogéniques, Mobrun, Noranda, Québec.

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# CALIBRATION OF THE ION MICROPROBE FOR THE DETERMINATION OF SILVER IN PYRITE AND CHALCOPYRITE FROM THE MOBRUN VMS DEPOSIT, ROUYN-NORANDA, QUEBEC

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## ABSTRACT

The silver contents of pyrite and chalcopyrite from the Mobrun volcanogenic massive-sulfide deposit near Noranda, Quebec, were determined using a Cameca IMS-4f ion microprobe. External standards of sulfides implanted with  $^{107}\text{Ag}$  were used for calibration. Secondary-ion yields obtained with  $\text{Cs}^+$  and  $\text{O}_2^+$  primary-beam sources were compared; the highest yields and best peak/background ratio were obtained with  $\text{O}_2^+$  and an energy offset of 90 V to eliminate mass interference by  $^{75}\text{As}^{16}\text{O}_2$  and  $^{75}\text{As}^{32}\text{S}$ . Minimum detection-limits (MDL) of 60 ppbw were routinely obtained, and are much lower than the MDL cited by previous investigators. Silver contents range from 0.1 to 1426 ppmw in pyrite and from 1 to 200 ppmw in chalcopyrite. Au/Ag values range from 0.002 to 1.273 in pyrite and from 0.001 to 1.000 in chalcopyrite. Silver contents of primary pyrite deposited by synvolcanic hydrothermal fluids are higher than those of secondary recrystallized pyrite formed during metamorphism and deformation, indicating that metamorphic recrystallization led to the release of silver from pyrite. The remobilized silver was deposited subsequently in tectonic veins in secondary chalcopyrite and with gold as electrum.

**Keywords:** secondary-ion mass spectrometry, ion microprobe, relative sensitivity factor, pyrite, chalcopyrite, silver, electrum, Au/Ag values, remobilization, Mobrun, Noranda, Quebec.

## SOMMAIRE

Les concentrations d'argent dans la pyrite et la chalcopyrite du gîte de sulfures massifs de Mobrun, près de Noranda, Québec, ont été déterminées avec une microsonde ionique Cameca IMS-4f. Nous avons utilisé, comme étalons externes, des sulfures implantés avec l'isotope  $^{107}\text{Ag}$ . Nous avons dû évaluer le taux de production des ions secondaires à partir de deux sources du faisceau d'ions primaires,  $\text{Cs}^+$  et  $\text{O}_2^+$ . C'est avec le  $\text{O}_2^+$  que nous avons réalisé les flux et les rapports de pics à bruit de fond les plus élevés, en utilisant un décalage en énergie de 90 V pour éliminer les interférences de masse avec  $^{75}\text{As}^{16}\text{O}_2$  et  $^{75}\text{As}^{32}\text{S}$ . Un seuil de détection minimum établi à 60 ppbw a couramment été atteint, ce qui est de beaucoup inférieur au seuil d'autres chercheurs. Les concentrations d'argent varient de 0.1 à 1426 ppmw dans la pyrite, et de 1 à 200 ppmw dans la chalcopyrite. Les valeurs Au/Ag varient de 0.002 à 1.273 dans la pyrite, et de 0.001 à 1.000 dans la chalcopyrite. Les teneurs d'argent dans la pyrite primaire, déposée par les fluides synvolcaniques hydrothermaux, sont plus élevées que celles de la pyrite recrystallisée pendant le métamorphisme et la déformation. Cette observation fait penser que l'argent a été lessivé au cours de la recrystallisation métamorphique. L'argent remobilisé a par la suite été déposé dans des veines d'origine tectonique dans la chalcopyrite secondaire et sous forme d'alliage de Au-Ag (électrum).

**Mots-clés:** spectrométrie de masse des ions secondaires, microsonde ionique, facteur de sensibilité relative, pyrite, chalcopyrite, argent, électrum, valeur Au/Ag, remobilisation, Mobrun, Noranda, Québec.

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# GSA TODAY

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## INSIDE

- Call for Nominations, p. 253
- Southeastern Section Meeting, p. 256
- North-Central-South-Central Sections Meeting, p. 257

## Gold Degassing and Deposition at Galeras Volcano, Colombia

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## ABSTRACT

Analyses of hydrothermally  
altered rocks, vein ore, 1992–1993  
andesite, 200–360 °C fumarole dis-

water (Heald et al., 1987; Hedenquist,  
1987; Rye, 1993). Geologic and geo-  
chemical characteristics of high-sulfida-  
tion Au deposits have been recently  
tabulated by White (1991). Such

tion in high-sulfidation deposits  
(Brimhall and Ghiorso, 1983; Giggen-  
bach, 1992; Rye, 1993; Hedenquist et  
al., 1993).

The highly active Colombian

the present formation of gold-enargite  
deposits at Galeras.

## GALERAS VOLCANO



**Figure 1.** The active cone within the Galeras crater looking west on January 25, 1993; the inner crater is about 500 m in diameter, and the cone height is about 150 m. Large andesite blocks as much as 5 m high were mostly vented during the July 16, 1992, explosion of the plug dome. Small fragments of hydrothermally altered vent breccia are also found on the cone. Deforms fumarole (200 °C) is the highly focused magmatic gas plume on the left edge of the inner crater.



## Gold Distribution in the Mobrun Volcanic-Associated Massive Sulfide Deposit, Noranda, Quebec: A Preliminary Evaluation of the Role of Metamorphic Remobilization

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### Abstract

The Mobrun Zn-Cu-Au-Ag orebodies show metal zonation typical of volcanic-associated massive sulfide deposits, although some metamorphic remobilization of metals has occurred. The nature and distribution of primary facies are the result of synvolcanic deposition and reworking of sulfides by hydrothermal fluids. Secondary facies resulting from metamorphism and deformation locally overprint primary facies and include transgressive veins which contain remobilized Au as electrum. The distribution of secondary facies was controlled by the mechanical properties of the mineralization as well as of the surrounding rocks; the mechanical response of different facies to deformation influenced the development and distribution of zones containing easily recoverable gold. Preservation of primary textures is best in the Main and Satellite lenses. The 1100 lens also shows significant preservation of primary facies; however, development of secondary facies is pronounced. Textural, structural, and chemical evidence indicates that the 1100 lens was subjected to more extreme metamorphic recrystallization and deformation than the other lenses. Metamorphic remobilization was important in releasing refractory Au from sulfides and locally concentrating it in a recoverable form (electrum).

### Introduction

THE most important sources of gold in Canada, both historically and currently, are the large deposits of Archean greenstone belts. The greatest concentration of these deposits is in the southern part of the Abitibi greenstone belt. The deposits can be divided into two principal types: shear-related vein and replacement deposits which formed late in the geologic development of the host greenstone belt (e.g., Hollinger-McIntyre deposit) and volcanic-associated massive sulfide deposits which formed early in the geologic development of the host greenstone belt (e.g., Horne, Bousquet) and which contain gold.

The origin of gold in Archean volcanic-associated massive sulfide deposits is controversial, and three main views are held: (1) gold was introduced syngenetically, its present distribution being the result of sea-floor hydrothermal processes (e.g., Huston and Large, 1989); (2) gold was introduced syngenetically, but its present distribution is the result of remobilization which occurred during metamorphism and tectonic deformation (e.g., Tourigny et al., 1989); and (3) gold was introduced epigenetically (probably postpeak metamorphism and postdeformation), as in most shear-related gold-only deposits

(e.g., Marquis et al., 1990). The main purpose of this paper is to describe the distribution of gold and metals within the Mobrun volcanic-associated massive sulfide deposit in relation to various facies of mineralization. In addition, we discuss the possibility that gold was introduced syngenetically and was subsequently remobilized during metamorphism and tectonic deformation.

The Mobrun mine is a good location to carry out a study of the controls on gold mineralization in volcanic-associated massive sulfide deposits for a number of reasons. Continuous hydrothermal activity led to the development of several stratigraphically stacked ore lenses (Fig. 1) of varying grades and tonnage of metals (Table 1). In terms of Au grades, Mobrun is in the upper 20 percent of volcanic-associated massive sulfide deposits in northwestern Quebec (Chartrand and Cattalani, 1990). The deposit has undergone greenschist facies metamorphism and deformation, and at least local-scale remobilization of sulfides has been documented (Caumartin and Caillé, 1990).

The exploration history, stratigraphic setting, alteration, structure, and geochemistry of host rocks of the Mobrun deposit have been described by previous workers (e.g., Caumartin and Caillé, 1990; Riopel et al., 1990; Barrett et al., 1992); a brief summary of the deposit geology is included here.

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## Carbonate-rich Footwall Alteration at the Mobrun Mine, a Possible Mattabi-type VMS Deposit in the Noranda Camp

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**Abstract** — The Mobrun VMS deposit in northwestern Quebec does not fit the classic Noranda-type model, but exhibits characteristics more consistent with a Mattabi-type deposit. The orebodies are underlain by fragmental volcanic rocks indicative of explosive volcanism in shallow water. Felsic volcanic rocks are more abundant than mafic rocks. Alteration assemblages comprise chlorite, carbonate, sericite, and quartz. Broad semi-conformable alteration occurs high in the footwall to the 1100 lens. Mobrun occurs higher in the stratigraphic sequence than most of the other deposits in the Noranda camp. In this part of the stratigraphy, zones of pervasive carbonatization may be more useful guides for exploration than zones of silicification.

### Introduction

Alteration zones associated with Archean volcanic-associated massive sulfide (VMS) deposits are more extensive than the deposits themselves and, therefore, represent important targets for exploration. Descriptive and genetic models of VMS deposits may be useful in exploration; however, it is necessary constantly to refine and re-evaluate models as new data are obtained. For example, there is increasing evidence that some deposits within the Noranda camp are inconsistent with the classic Noranda-type model (Chartrand and Cattalani, 1990). This paper describes some geological characteristics of the Mobrun deposit, located 20 km northeast of Rouyn-Noranda, which are not typical of Noranda-type deposits. Operating control of the deposit has recently been acquired by Cambior Inc. from Audrey Resources Inc.

### Classification of Archean VMS Deposits

Morton and Franklin (1987) subdivided Archean Cu-Zn VMS deposits into Mattabi-type and Noranda-type, based on differences in the composition and physical characteristics of volcanic rocks, and the nature and distribution of alteration mineral assemblages. A brief summary of the relevant characteristics of each type compiled from various sources (Franklin, 1984, 1986; Franklin et al., 1981; Morton, 1984; Morton and Franklin, 1987; Osterberg et al., 1987) follows.

**Noranda-type deposits** are underlain by volcanic sequences dominated by rocks of mafic composition. Conspicuously lacking are rocks formed by hydrovolcanic explosions, indicating that extrusive activity occurred at water depths greater than approximately 500 m. Alteration pipes beneath Noranda-type deposits are well defined, consisting of an inner zone of chlorite + quartz and an outer zone consisting of sericite and quartz. Semi-conformable altera-

tion zones of silicified and spilitized rocks are laterally and vertically extensive, and tend to be controlled by permeable units in the volcanic sequence. Semi-conformable alteration is characteristically earlier than, and may be crosscut by, pipe alteration.

**Mattabi-type deposits** are underlain dominantly by felsic fragmental rocks such as hydrovolcanic tuffs, pyroclastic flows, hyaloclastites, and flow breccias. The amygdule content of lava flows is relatively high. Fragmental rocks are commonly formed from the explosive interaction between water and magma in a shallow subaqueous or subaerial environment (water depths less than ~500 m). Alteration pipes are poorly defined, not distinctly zoned, and consist of variable amounts of iron-bearing carbonates, dolomite, calcite, iron chlorite, sericite, alumino-silicates (andalusite, kyanite, pyrophyllite) and quartz. Chloritoid is present in greenschist-grade metamorphic rocks, especially along synvolcanic faults and in adjacent laterally extensive semi-conformable alteration zones. The semi-conformable alteration zones may extend up to the ore zone, and merge with the pipe-shaped zone of alteration. Semi-conformable alteration zones consist of patches of highly metasomatized rock, distributed along zones of high permeability in the host rock sequence. The mineralogy of the semi-conformable and pipe-shaped alteration zones are similar. Carbonate alteration in some cases preceded sericite and chlorite formation.

The dominant factors controlling the type of Archean VMS deposit that formed appear to have been water depth, and the bulk composition and physical characteristics of the footwall volcanic rocks (Morton and Franklin, 1987).

### Mobrun VMS Deposit

The Mobrun deposit comprises three massive sulfide complexes: the Main lens, the Satellite lens complex and the 1100 lens complex (Fig. 1). All that is known about the stratigraphy and structure at Mobrun, and most of the data on



# Zonation of secondary minerals in hydrothermally altered seafloor lavas from the Galapagos Rift

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Larocque, A.C.L., Jonasson, I.R., and LeCheminant, G.M., Zonation of secondary minerals in hydrothermally altered seafloor lavas from the Galapagos Rift; in *Current Research, Part F, Geological Survey of Canada, Paper 89-1F*, p. 9-15, 1989.

## Abstract

An extinct hydrothermal system that formed a massive Cu-Zn sulphide deposit is exposed on a horst block in the eastern Galapagos Rift. Samples collected from the hydrothermal alteration and stockwork zone exhibit pronounced compositional and textural zonation of secondary minerals. A basaltic andesite hyaloclastite bed consists of shards composed of micron- to millimetre-scale bands of chlorite, cristobalite, and smectite. Altered pillow fragments from a glassy Fe-Ti basalt flow contain chlorite, kaolinite, quartz, and illite-smectite, and exhibit zonation of primary quench textures. Differences in protolith composition and original permeability of the samples may have contributed to the differences in composition, type, and scale of alteration.

## Résumé

Un système hydrothermal éteint qui a entraîné la formation d'un gisement de sulfures massifs cupro-zincifères est mis à nu sur un massif soulevé dans la partie est du fossé d'effondrement des Galapagos. Des échantillons prélevés dans la zone d'altération hydrothermale et de fissures minéralisées présentent une zonation marquée de la composition et de la texture des minéraux accessoires. Une couche d'andésite basaltique hyaloclastique est formée d'éclats composés de bandes de chlorite, de cristobalite et de smectite dont la taille varie de l'ordre du micron au millimètre. Des fragments en coussins altérés d'une coulée de basalte vitreuse contenant Fe et Ti renferment de la chlorite, de la kaolinite, du quartz et de l'illite et smectite, et présentent une zonation de textures de trempe primaires. Des différences au niveau de la composition de la roche-mère et de la perméabilité originelle des échantillons peuvent avoir contribué à produire les différences observées au niveau du type et du degré d'altération ainsi qu'au niveau de la composition des roches altérées.

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