

Geochemical and Sulfur-Isotopic Signatures of Volcanogenic Massive Sulfide Deposits on Prince of Wales Island and Vicinity, Southeastern Alaska

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Abstract

Stratabound volcanogenic massive sulfide (VMS) deposits on Prince of Wales Island and vicinity, southeastern Alaska, occur in two volcanosedimentary sequences of Late Proterozoic through Cambrian and of Ordovician through Early Silurian age. This study presents geochemical data on sulfide-rich samples, in situ laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of sulfide minerals, and sulfur-isotopic analyses of sulfides and sulfates (barite) for identifying and distinguishing between primary sea-floor signatures and later regional metamorphic overprints. These datasets are also used here in an attempt to discriminate the VMS deposits in the older Wales Group from those in the younger Moira Sound unit (new informal name). The Wales Group and its contained VMS deposits have been multiply deformed and metamorphosed from greenschist to amphibolite grade, whereas the Moira Sound unit and related VMS deposits are less deformed and generally less metamorphosed (lower to middle greenschist grade). Variations in the sulfide mineral assemblages and textures of the VMS deposits in both sequences reflect a combination of processes, including primary sea-floor mineralization and sub-sea-floor zone refining, followed by metamorphic recrystallization. Very coarse grained (>1 cm diam) sulfide minerals and abundant pyrrhotite are restricted to VMS deposits in a small area of the Wales Group, at Khayyam and Stumble-On, which record high-grade metamorphism of the sulfides.

Geochemical and sulfur-isotopic data distinguish the VMS deposits in the Wales Group from those in the Moira Sound unit. Although base- and precious-metal contents vary widely in sulfide-rich samples from both sequences, samples from the Moira Sound generally have proportionately higher Ag contents relative to base metals and Au. In situ LA-ICP-MS analysis of trace elements in the sulfide minerals suggests that primary sea-floor hydrothermal signatures are preserved

in some samples (for example, Mn, As, Sb, and Tl in pyrite from the Moira Sound unit), whereas in other samples the signatures are varyingly annealed, owing to metamorphic overprinting. A limited LA-ICP-MS database for sphalerite indicates that low-Fe sphalerite is preferentially associated with the most Au rich deposits, the Niblack and Nutkwa.

Sulfur-isotopic values for sulfide minerals in the VMS deposits in the Wales Group range from 5.9 to 17.4 permil (avg 11.5 ± 2.7 permil), about 5 to 6 permil higher than those in the Moira Sound unit, which range from -2.8 to 10.4 permil (avg 6.1 ± 4.0 permil). This difference in $\delta^{34}\text{S}_{\text{sulfide}}$ values reflects a dominantly seawater sulfate source of the sulfides and is linked to the $\delta^{34}\text{S}$ values of contemporaneous seawater sulfate, which were slightly higher during the Late Proterozoic through Cambrian than during the Ordovician through Early Silurian.

Introduction

Stratabound volcanogenic massive sulfide (VMS) deposits occur worldwide in metasedimentary and metavolcanic rocks of Archean through Tertiary age (for example, Barrie and Hannington, 1999; Franklin and others, 2005). These commercially important mineral deposits form by submarine hydrothermal processes on and beneath the sea floor, depositing Fe, Cu, Zn, and (or) Pb sulfide minerals that in places are accompanied by economic amounts of Ag, Au, Sn, and other metals. In southeastern Alaska, VMS deposits are recognized in three major lithostratigraphic belts of Late Proterozoic through Cambrian, Ordovician through Silurian, and Triassic age that extend discontinuously from northwest of Haines in the north to Prince of Wales Island in the south (Newberry and others, 1997b). The Triassic deposits, which currently are the most important economically, include the polymetallic Greens Creek Zn-Pb-Cu-Ag-Au massive sulfide ore body that presently is being mined on Admiralty Island, ~250 km northwest of Prince of Wales Island (Taylor, 1997; Newberry and Brew, 1999; Taylor and others, 1999).

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In this study, we report geochemical and sulfur-isotopic analyses of samples of massive and semimassive sulfides from the two older groups of VMS deposits and occurrences on southern Prince of Wales Island and vicinity (fig. 1). These data are used here together with geologic and textural features to better characterize the metallogeny of the deposits and to provide an analytical framework for potentially discriminating the Late Proterozoic through Cambrian from the Ordovician through Silurian VMS deposits in the region.

Geologic and Metallogenic Setting

Prince of Wales and surrounding islands (fig. 1) are underlain by a wide variety of stratified and intrusive rocks of Late Proterozoic through Tertiary age (Gehrels and Saleeby,

1987; Gehrels, 1990, 1992; see Karl and others, this volume) that constitute part of the regionally extensive Alexander terrane, which extends from eastern Alaska and southwestern Yukon Territory southward into southeastern Alaska and coastal British Columbia (for example, McClelland and others, 1992; Karl and others, 1999; Nokleberg and others, 2001). On Prince of Wales Island and vicinity, the oldest unit is the Upper Proterozoic through Cambrian Wales Group, which comprises various deformed metavolcanic and lesser metasedimentary rocks, including greenstone and amphibolite, felsic schist and gneiss, graphitic phyllite, minor marble, and sparse metaconglomerate (see Karl and others, this volume). The Wales Group also hosts most of the VMS deposits in the study area. The age of the Wales Group is constrained mainly by a concordant U-Pb zircon age of 554 ± 4 Ma for a crosscutting granitic (now orthogneiss) pluton on southern Dall Island (fig. 1; Gehrels, 1990). A maximum age for the Wales Group

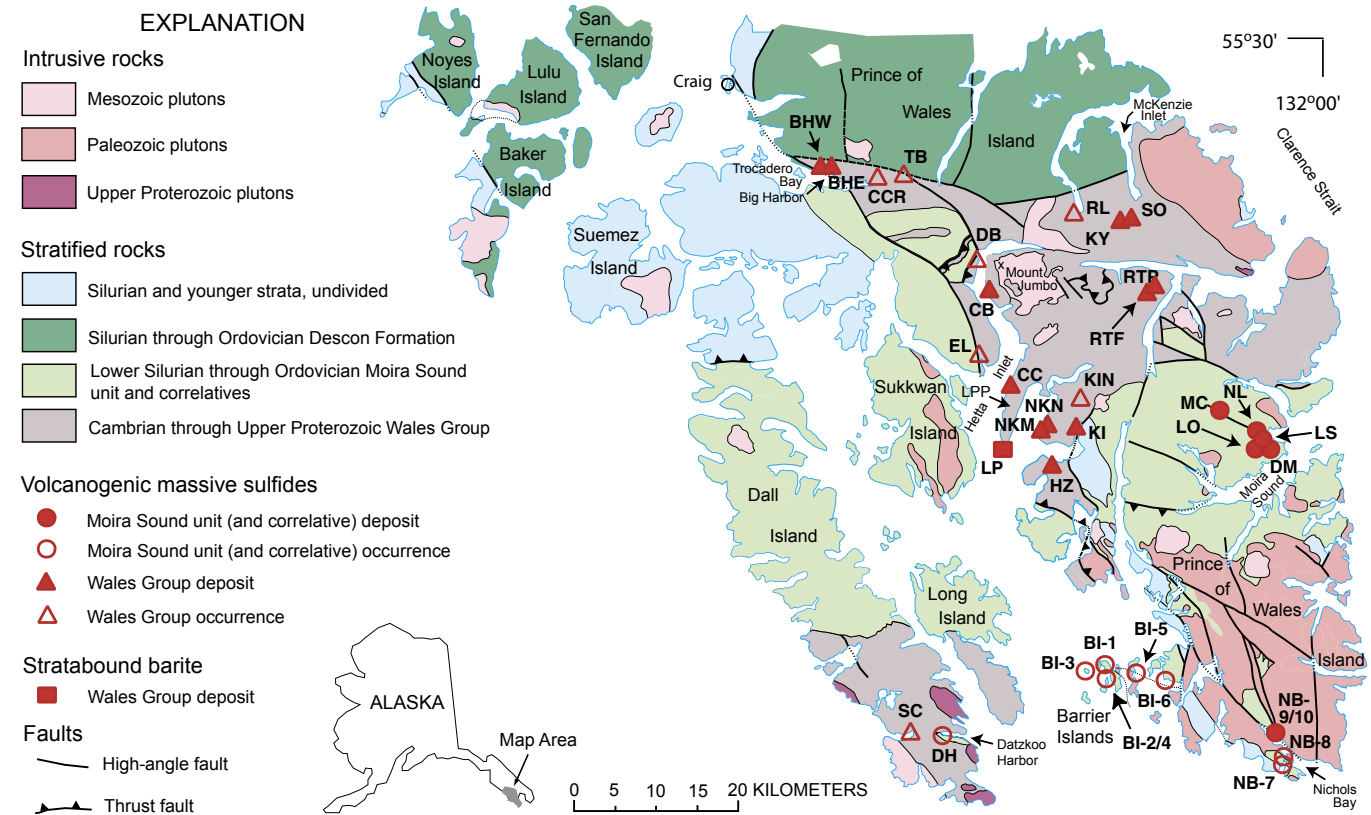


Figure 1. Simplified geologic map of southern Prince of Wales Island and vicinity, showing locations of volcanogenic massive sulfide deposits and occurrences in study area. Geology from Karl and others (this volume). Deposits and occurrences: BHE, Big Harbor East; BHW, Big Harbor West; BI, Barrier Islands; CB, Corbin; CC, Copper City; CCR, Cable Creek roadcut; DB, Deer Bay; DH, Datzkoo Harbor; DM, Dama; EL, Eek Lake; HZ, Hozer; KI, Keete Inlet; KIN, Keete Inlet North; KY, Khayyam; LO, Lookout Mountain; LP, Lime Point (barite); LS, Lindsay/88; MC, Moira Copper; NB, Nichols Bay; NKM, Nutkwa Main; NKN, Nutkwa North; NL, Niblack; RL, Rock Lake; RTF, Ruby Tuesday (Fish Show; includes the Chomly deposit); RTP, Ruby Tuesday (Polymetal); SC, Security Cove; SO, Stumble-On; TB, Trocadero Bay. In the Niblack area, the Trio and Broadgauge deposits (not shown) are located between the Dama and Lindsay/88 deposits. Numbered suffixes for Barrier Islands (BI-1 through BI-6) and Nichols Bay (NB-7 through NB-10) deposits and occurrences (table 1) correspond to those used by Gehrels and others (1983). Note that thick limestone and dolostone of the Moira Sound unit on Dall and Long Islands are not distinguished from other rock types in this sequence.

is estimated at 600 m.y. on the basis of U-Pb geochronology of igneous zircons from apparently coeval plutons and of detrital zircons from younger strata (see Karl and others, this volume). Rocks of the Wales Group, together with several enclosed plutons, were deformed and regionally metamorphosed twice, in the Early Ordovician and Early Devonian. Geochemical studies of mafic metavolcanic rocks in the Wales Group reveal mainly transitional to midocean-ridge basalt (MORB) magmatic signatures that suggest formation in an oceanic-arc terrane (Barrie and Kyle, 1988; see Karl and others, this volume). Lead-isotopic values for sulfide minerals in the VMS deposits in the Wales Group are relatively unradiogenic, consistent with a primitive-arc setting for these deposits and their volcanosedimentary host sequence (see Ayuso and others, this volume).

Younger stratified metavolcanic and metasedimentary rocks of the Moira Sound unit (new informal name), which are dated at Early Ordovician through Silurian (see Karl and others, this volume), are economically important because, like the Wales Group, they also contain VMS deposits and occurrences. The Moira Sound unit consists dominantly of siltstone, mudstone, graywacke turbidite, and carbonaceous argillite, alternating with thick sections of mafic, intermediate-composition, and silicic volcanic rocks and minor conglomerate and limestone. Graptolites and conodonts range in age from late Early Ordovician to Early Silurian. The oldest dated pluton that intrudes the Moira Sound unit is a 472 ± 5 -m.y.-old granodiorite on southern Prince of Wales Island (Gehrels and Saleeby, 1987), which probably was emplaced into the lower part of this sequence contemporaneously with deposition of the upper part of the Moira Sound unit; the youngest dated pluton that intrudes this unit, in Moira Sound, has a U-Pb zircon age of 427 ± 4 m.y. (R. Friedman, written commun., 2004). Geochemical data for the mafic volcanic rocks indicate mainly calc-alkaline petrologic affinities that imply deposition in an island-arc setting (see Karl and others, this volume).

Most younger strata in the study area (fig. 1) are dominated by sedimentary rocks. The widespread Descon Formation, of Middle Ordovician through Silurian age, comprises volcanoclastic graywacke turbidite, siliceous shale, chert, and minor calc-alkaline to alkaline basalt and andesite but no rhyolite or dacite. Various other Silurian and Devonian sedimentary rocks also occur in the region. None of these sequences contains massive sulfide deposits. Unconformably overlying the Paleozoic strata are Tertiary sedimentary rocks, including coal, Tertiary through Quaternary basalt, and various alluvial, colluvial, and glacial deposits.

Three major tectonometamorphic events affected Prince of Wales Island and vicinity. The first event was in the Late Proterozoic, as documented by 554-m.y.-old orthogneiss on Dall Island that cuts a preexisting fabric in rocks of the Wales Group (Gehrels, 1990). The second event was in the Early Ordovician, after deposition of the Wales Group but before deposition of the Moira Sound unit. This event produced isoclinal to recumbent folds and a regional metamorphic grade ranging from lower greenschist to upper amphibolite facies

(Gehrels and Saleeby, 1987; Gehrels, 1990). Peak conditions during this Ordovician metamorphism were temperatures of 610–690°C and pressures of 8.4 to 10.1 kbars (Zumsteg and others, 2004). The third major event, which occurred in the Early Devonian as dated by Ar-Ar geochronology (see Karl and others, this volume), followed deposition of the Moira Sound unit and the Descon Formation, generating open folds, slaty cleavage, and greenschist-facies mineral assemblages. Peak metamorphic conditions during this event were a temperature of ~535°C and a pressure of 6.8 kbars (Zumsteg and others, 2004). Rocks of the Wales Group are generally recognizable by the presence of two periods of penetrative deformation (for example, F2 folds), in contrast to the single period of deformation that characterizes the Moira Sound unit (see Karl and others, this volume).

Plutonic rocks in the region are abundant and vary widely in age and petrology. Geologic and geochronologic data indicate ages of Late Proterozoic, Ordovician, Silurian, Devonian, Permian, Jurassic, and Cretaceous (Gehrels and Saleeby, 1987; see Karl and others, this volume) and compositions ranging from granite, through syenite, to gabbro and pyroxenite. Some of the Paleozoic and Mesozoic plutons are genetically related to economically important magmatic-hydrothermal ore deposits, including the Devonian Kasaan and the Cretaceous Jumbo-Copper Mountain Fe-Cu-Au skarns (Wright, 1915; Newberry and others, 1997a), the Devonian through Silurian Salt Chuck Cu-Au-Ag-Pd-Pt deposit (Watkinson and Melling, 1992; Foley and others, 1997), and the Jurassic Bokan Mountain U-Th-rare-earth-element-Nb-Ta dike system (Thompson, 1988; Foley and others, 1997). Small posttectonic base- and precious-metal veins are widespread in the region, some of which are spatially associated with the Paleozoic and Mesozoic plutons (Maas and others, 1995).

Faults are common throughout the study area (fig. 1; see Karl and others, this volume). Deformed thrust faults occur within the Wales Group and along its contacts with the younger Moira Sound unit; thrust faults also cut the Cretaceous pluton at Mount Jumbo (Herreid and others, 1978; see Karl and others, this volume). These relations indicate that thrusting occurred during Ordovician and Cretaceous and, possibly, other tectonic events. High-angle faults cut all major units, including many Late Proterozoic and Devonian plutons. Major regional strike-slip faults of Tertiary age on the east side of Prince of Wales Island (for example, in Clarence Strait) record transform faulting between the Pacific and North American Plates, after Jurassic through Cretaceous accretion of the Alexander terrane to the inboard terranes of southeastern Alaska and coastal British Columbia (Karl and others, 1999; Nokleberg and others, 2001).

Analytical Methods

Whole-rock compositions of samples of massive and semimassive sulfide were obtained by XRAL Laboratories in Denver, Colo. Major and minor elements were analyzed by

inductively coupled plasma atomic-emission spectrometry (ICP–AES) after acid digestion of powdered samples. Total S content was determined by Leco furnace methods, As, Sb, Hg, Se, Te, and Tl contents by atomic-absorption spectrometry, and Au content by fire assay. Analytical results are not reported for Nb, Ta, Cr, Ba, Sn, Th, Y, La, and Ce, which typically concentrate in resistate heavy minerals (for example, rutile, chromite, barite, cassiterite, monazite), because a flux was not used in the ICP–AES analyses to ensure their complete dissolution; similarly, data for Ti may not be meaningful (that is, are too low) and should be viewed with caution.

Trace-element contents in sulfide minerals were determined by laser-ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) at the U.S. Geological Survey (USGS) laboratory in Denver, Colo. This technique has the advantage of providing in situ analyses at low concentrations and high precision (for example, Watling and others, 1995; Ridley and Lichte, 1998; Butler and Nesbitt, 1999; Axelsson and Rodushkin, 2001). Polished thin sections were used for the LA–ICP–MS analyses to allow integration of the geochemical results with information on textures and mineral assemblages. Analyses were obtained for counting times of 5 minutes on 50- μ m-diameter spots, according to the methods of Ridley and Lichte (1998), using a synthetic sulfide standard, as described by Wilson and others (2002). Data reduction was done offline with GeoPro software (CETAC Technologies, 2000). This software program was used to select spectra that were unaffected by analysis of small mineral inclusions (for example, chalcopyrite in sphalerite), thus providing more robust data on the phase-specific trace-element contents of the sulfide minerals. Total analytical precision by the LA–ICP–MS method is estimated at 2 to 8 percent (Ridley, 2000; Norman and others, 2003).

Sulfur-bearing phases from mineralized samples were physically separated and analyzed for $\delta^{34}\text{S}$ values, using an automated elemental analyzer interfaced to an isotope-ratio mass spectrometer (Giesemann and others, 1994), at the USGS laboratory in Denver, Colo. The $\delta^{34}\text{S}$ values were calibrated to the Cañon Diablo troilite standard and are reported here in conventional permil notation; relative error is estimated at ± 0.2 permil. Disseminated sulfides in unmineralized host rocks were separated in bulk, using the CrCl_2 dissolution method of Tuttle and others (1986), which extracts all sulfide minerals. Barite from the Big Harbor West deposit (BHW, fig. 1) that is intergrown with fine-grained sulfides was separated by using the NaCO_3 method of Breit and others (1985) to permit analysis of barite only and not also admixed sulfides.

VMS Deposits

History and Production

VMS deposits and occurrences in the study area are restricted to Late Proterozoic through Cambrian rocks of the

Wales Group and Silurian through Ordovician rocks of the Moira Sound unit (fig. 1; table 1). In this report, VMS deposits are distinguished from occurrences by evidence at the deposits of past mining development or mineral exploration (for example, trenching, core drilling). The largest known deposits are the Khayyam and nearby Stumble-On ore bodies in the Wales Group, at the head of McKenzie Inlet, which were mined from 1901 to 1907, producing 210,000 t of massive sulfide ore averaging 1.7 weight percent Cu, 9.6 ppm Ag, and 1.9 ppm Au (Barrie, 1984; Barrie and Kyle, 1988). The Khayyam deposit (KY, fig. 1) has an additional estimated resource of 78,700 t of massive sulfide averaging 2.9 weight percent Cu, 0.8 weight percent Zn, 17 ppm Ag, and 1.3 ppm Au (Maas and others, 1995). The Copper City Mine (CC, fig. 1) produced 77 t Cu, 146 kg Ag, and 10.6 kg Au between 1903 and 1905; the Corbin Mine (CB, fig. 1) produced smaller amounts of Cu (9.7 t) and Ag (12 kg) during 1906–13 (Bufvers, 1967). The Niblack deposit (NL, fig. 1), in the Moira Sound unit on the north side of Moira Sound, was mined from 1902 to 1908, producing 18,000 t of ore averaging 4.9 weight percent Cu, 34 ppm Ag, and 2.3 ppm Au (Maas and others, 1995). Mineral exploration in the Niblack area from 1993 to 2006 has identified several more VMS deposits, including the Lookout Mountain deposit (LO, fig. 1), with an inferred resource of 2.52 Mt averaging 3.22 weight percent Zn, 1.70 weight percent Cu, 36.4 g Ag/t, and 2.77 g Au/t. The nearby Dama (DM, fig. 1), Lindsay/88 (LS, fig. 1), and Trio/Broadgauge deposits contain significant amounts of Zn, Cu, Ag, and Au in some drill holes (Adamson and Gray, 1995; Niblack Mining Corp., 2006, URL <http://www.niblackmining.com/>). Other VMS deposits on Prince of Wales Island and vicinity were not mined or have only minor reported production (Barrie and Kyle, 1988; Maas and others, 1995), estimated at no more than 500 t. During the 1990s, the Nutkwa deposits (NKM/NKN, fig. 1) were extensively explored and drilled, while the Big Harbor East and West, Copper City, Corbin, and Hozer deposits (BHE/BHW, CC, CB, and HZ, respectively, fig. 1) had only limited exploration and drilling.

Deposits in the Wales Group

The Khayyam and Stumble-On deposits (KY and SO, respectively, fig. 1) form elongate lenses of massive and semi-massive sulfide, as much as 6 m thick and at least 170 m long, within amphibolite-facies metavolcanic and metasedimentary rocks of the Wales Group (Fosse, 1946; Barrie, 1984; Barrie and Kyle, 1988). Major host rocks at and near these deposits include mafic and felsic schist and gneiss, intermediate-composition schist, and siliceous schist. Lenses of amphibolite and large bodies of both foliated and unfoliated diorite occur in the area. Thin (<1 cm thick) beds of cotecule (spessartine quartzite) are also present in some felsic schist and gneiss. Sulfide minerals are clearly recrystallized by postore regional metamorphism, typically forming a mixture of euhedral and granoblastic grains in which coarse-grained to very coarse grained (>1 cm diam) pyrite occurs within a matrix of chalc-

Table 1. Data for volcanogenic massive sulfide deposits and occurrences on southern Prince of Wales Island and vicinity, southeastern Alaska.

[Numbered Barrier Islands occurrences correspond to locations in Gehrels and others (1983). Longitudes in parentheses are approximate. Host rocks, listed in decreasing order of abundance: amp, amphibolite; bas, basalt or metabasalt (including greenstone, andesite, and chlorite schist); bs, black shale and slate; cht, chert or metachert; cot, coticule; dol, dolomite; fels, felsic schist and gneiss (including quartz-sericite schist and volcanoclastic sedimentary rocks); gab, gabbro or metagabbro (including diorite and quartz diorite); grn, granite; grw, graywacke; if, iron-formation; jas, jasper; mbl, marble; phy, phyllite; rhy, rhyolite or metarhyolite (including tuff, breccia, and conglomerate); sh, shale and slate (including argillite). Principal metals are listed in decreasing order of concentration in production records or chemical analyses (Maas and others, 1995; this study). Opaque minerals, listed in decreasing order of abundance: asp, arsenopyrite; bn, bornite; cp, chalcopyrite; gl, galena; mt, magnetite; po, pyrrhotite; py, pyrite; sl, sphalerite]

Deposit or occurrence (fig. 1)	Latitude (°N.)	Longitude (°W.)	Host rocks	Principal metals	Opaque minerals	Major reference
Wales Group						
Khayyam -----	55.29861	132.38611	fels, amp, gab, cot	Cu, Zn, Ag, Au	py, cp, sl, po, asp, mt	Barrie and Kyle (1988).
Stumble-On -----	55.29583	132.37222	fels, amp, gab	Cu, Zn, Ag, Au	py, cp, sl, po, asp, mt	Do.
Rock Lake -----	55.30833	132.50000	fels, amp	Cu, Zn, Au	py, cp, sl, mt	Barrie (1984).
Big Harbor East -----	55.37611	132.95361	fels, bas, sh	Cu, Ag, Au	py, cp	Maas and others (1995).
Big Harbor West -----	55.37556	132.96389	bas, fels, sh	Cu, Zn, Ag, Au	py, cp, sl	Do.
Ruby Tuesday (Polymetal) -----	55.21667	132.32278	fels, bas, cht, mbl	Zn, Pb, Cu, Ag	py, sl, gl, cp	Kucinski (1987).
Ruby Tuesday (Fish Show) -----	¹ 55.22167	132.33528	fels, bas, cht, mbl	Zn, Pb, Cu, Ag	py, sl, gl, cp	Maas and others (1995).
Copper City -----	55.13417	132.60944	rhy, phy, bas, if, jas	Cu, Zn, Ag, Au	py, cp, sl, gl, mt	Thurston (1994).
Eek Lake -----	55.17042	132.67375	rhy, fels, bas	Cu	py, cp	Casselmann and Bohme (1997).
Corbin -----	55.23139	132.64861	fels, rhy, phy	Cu, Zn, Ag, Au	py, cp, sl	Thurston (1994).
Keete Inlet -----	55.08111	132.48889	fels, rhy, bas, if	Cu, Zn, Ag, Au	py, cp, sl, bn, mt	Maas and others (1991).
Keete Inlet North -----	55.10986	132.47561	fels, rhy, bas	Cu, Zn, Ag, Au	py, cp, sl	Do.
Nutkwa Main -----	55.07653	132.55128	rhy, fels, bas	Zn, Cu, Pb, Ag	py, sl, cp, gl	Casselmann and Bohme (1997).
Nutkwa North -----	55.08681	132.54153	rhy, fels, bas	Zn, Cu, Pb, Ag	py, sl, cp, gl	Do.
Hozer -----	55.04000	132.54250	fels, rhy, bas	Zn, Cu	py, sl, cp	Maas and others (1991).
Deer Bay exhalite -----	55.26917	132.66667	fels, bas, phy	Cu, Zn, Ag, Au	py, cp, sl	Maas and others (1995).
Cable Creek roadcut -----	55.35179	132.83060	fels, phy, bas	Cu, Zn, Ag, Au	py, sp, sl	Do.
Trocadero Bay exhalite -----	55.35849	132.82680	fels	None identified	py	Do.
Security Cove (Dall Island) -----	54.75000	132.85694	fels, bas, mbl	Zn, Pb, Ag, Ba	py, sl, gl, cp	Maas and others (1995).
Moira Sound unit and correlatives						
Niblack -----	55.06667	132.14639	rhy, bas, if, jas, cht	Cu, Zn, Ag, Au	py, cp, sl	Peek (1975).
Lookout Mountain -----	55.05639	132.14139	rhy, bas	Zn, Cu, Ag, Au	py, sl, cp	Niblack Mining Corp (2006).
Dama -----	55.05389	132.12528	rhy, bas	Zn, Cu, Ag, Au	py, sl, cp	Adamson and Gray (1995).
Lindsay/88 -----	55.06306	132.13833	rhy, bas	Zn, Cu, Ag, Au	py, sl, cp	Do.
Moira Copper -----	55.07644	132.17987	rhy, bas	Cu, Ag, Au	py, cp, mt	Wright and Wright (1908).
Barrier Islands No. 1 -----	54.81222	132.44889	bas, rhy, bs	Zn, Ba	py, sl	Gehrels and others (1983).
Barrier Islands No. 2 -----	54.80139	132.45464	rhy, bas	Zn, Pb, Ag	py, sl, gl	Do.
Barrier Islands No. 3 -----	54.81000	132.49472	rhy, bas	None identified	py	Do.
Barrier Islands No. 4 -----	54.79722	132.45056	rhy, bs, bas, dol	None identified	py	Do.
Barrier Islands No. 5 -----	54.80389	132.39167	rhy, gab	None identified	py	Do.
Barrier Islands No. 6 -----	54.79722	132.33833	bs, rhy	None identified	py	Do.
Nichols Bay No. 7 and 8 -----	54.70237	132.11715	rhy, bas	None identified	py	Do.
Nichols Bay No. 9 and 10 -----	² 54.73514	132.14154	grw, bs, rhy, grn	Zn, Ag	po, py, sl, mt	Do.
Datzkoo Harbor (Dall Island) ----	54.74056	132.74944	fels, bas	Zn, Ag, Ba	py, sl	Maas and others (1995).

¹Includes the nearby Chomly deposit ~500 m to the west (Kucinski, 1988; Maas and others, 1995).

²These small deposits occur within the contact aureole of a Silurian(?) granite (see Karl and others, this volume).

pyrite, pyrrhotite, and (or) sphalerite (figs. 2A, 2B, 3A). Some samples contain abundant granoblastic sphalerite, especially at the Stumble-On deposit (fig. 2C); pyrrhotite is common at both deposits. Among all the VMS deposits on Prince of Wales Island and vicinity, the Khayyam and Stumble-On deposits have the coarsest grained sulfide minerals.

Massive sulfides at the Corbin deposit (CB, fig. 1) occur within a deformed sequence of lower-greenschist-facies rhyolitic tuff and tuffaceous sedimentary rocks (Wright and Wright, 1908; Maas and others, 1995). A schist unit containing distinctive pink piemontite (Mn-epidote) is locally present in the footwall (Thurston, 1994; Hattie and others, 1996). The sulfide ore body is as much as 1 m thick and at least 75 m long. Detailed surface and underground mapping reported by Thurston (1994) reveals complex structures within the massive sulfides, including isoclinal folds and shear zones. Massive granoblastic pyrite is widespread, accompanied by varying amounts of chalcopyrite and sphalerite that in places define a conspicuous mineralogical layering (fig. 3B).

VMS deposits in the Big Harbor area (fig. 1) occur in two main areas on the north side of Trocadero Bay (Chapin, 1916; Twenhofel and others, 1949). The deposits are within a greenschist-facies sequence of tightly folded quartz-sericite schist, metabasaltic greenstone, and dacitic tuff that are spatially associated with an elongate body of feldspar porphyry (Terry and Gibson, 1998). The Big Harbor East deposit (BHE, fig. 1) consists mainly of siliceous pyritic sulfide, as much as 9 m thick, containing varying amounts of matrix chalcopyrite and minor sphalerite and sericite. About 750 m to the west, the Big Harbor West deposit (BHW, fig. 1) forms a nearly 1-m-thick stratiform lens of massive chalcopyrite and minor pyrite and sphalerite (fig. 3C) within greenstone and quartz-sericite schist. A thin stratiform unit about 150 m to the north, composed of Mn-calcite and spessartine garnet, minor quartz, barite, magnetite, and galena, and sparse sphalerite and chalcopyrite, probably represents an exhalative chemical sediment in the upper hanging-wall sequence (Terry and Gibson, 1998).

The small Keete Inlet deposit (KI, fig. 1) consists of massive siliceous pyritic sulfide with minor chalcopyrite, sphalerite, and rare bornite, hosted in metarhyolitic tuff and metabasaltic greenstone (Chapin, 1916; Maas and others, 1991). Massive sulfide layers are as much as 0.6 m thick. Common textures show granoblastic pyrite within a matrix of fine-grained chalcopyrite and sphalerite (figs. 2D, 3D). A thin unit of magnetite iron-formation, which occurs in shoreline outcrops several hundred meters south of the deposit (see Karl and others, this volume), may be related to the sulfide mineralization. Metamorphic grade in the area is lower to middle greenschist facies. A similar but smaller VMS occurrence, here designated Keete Inlet North (KIN, fig. 1), is about 3.4 km north-northeast of the main deposit (Maas and others, 1991).

The Copper City (also known as Red Wing) deposit (CC, fig. 1) consists of a massive sulfide layer, as much as 2 m thick and nearly 100 m long, within a sequence of mainly

felsic metavolcanic and metasedimentary rocks (Wright and Wright, 1908; Herreid and others, 1978). Footwall strata are composed of sericite-altered metarhyolite and metadacite with thin interbeds of mafic metatuff; the hanging wall contains jasper, magnetite iron-formation, and ferruginous micaceous phyllite (Wright and Wright, 1908; Thurston, 1994; Maas and others, 1995). Thurston (1994) and Forbes and others (1995) also reported a 0.3-m-thick pink layer in the hanging wall that contains abundant piemontite. Sulfide minerals consist mainly of pyrite and chalcopyrite, minor sphalerite, and rare galena (figs. 2E, 3E). As much as 6,700 ppm Ba occurs in some sulfide-rich samples (Maas and others, 1995, table A-2), but whether this element resides in minor barite or in Ba-feldspar or mica is unknown. To the northwest, across Hetta Inlet, the Eek Lake occurrence (EL, fig. 1) is a small lens, less than 0.3 m thick, composed of pyrite and abundant chalcopyrite within altered felsic metavolcanic rocks (Casselmann and Bohme, 1997).

The only true polymetallic VMS deposits on Prince of Wales Island and vicinity (fig. 1) are in the Ruby Tuesday area. Several VMS deposits have been identified here, including the Chomly, Fish Show, and Polymetal; the first two (RTF, fig. 1) are about 1.5 km west-northwest and 1 km northwest, respectively, of the Polymetal deposit (RTP, fig. 1; Fowler, 1949; Kucinski, 1987; Maas and others, 1995). The deposits occur at two or, possibly, three different stratigraphic levels, in a folded and faulted volcanosedimentary sequence with a lower-greenschist-facies metamorphic overprint. The Polymetal deposit is in locally fragmental felsic volcanoclastic schist, whereas the Chomly and Fish Show deposits are in siliceous graphitic argillite. Metabasaltic greenstone and marble also occur in parts of the Ruby Tuesday area (Kucinski, 1987). Massive sulfide from the Fish Show deposit is noteworthy in containing conspicuous volcanic clasts within a matrix of fine-grained sphalerite, galena, pyrite, and minor chalcopyrite (figs. 2F, 3F).

Two main areas of massive sulfide are known in the Nutkwa area (Nutmwa Main and North deposits; NKM/NKN, fig. 1), west of the Keete Inlet deposit (KI, fig. 1). The Nutkwa deposits occur in a sequence of lower-greenschist-facies, dacitic to rhyolitic volcanic rocks and volcanoclastic sedimentary rocks, together with varying amounts of metabasaltic greenstone (Hattie and others, 1996; Casselman and Bohme, 1997). Massive sulfides at both deposits are in stratiform layers, 0.3 to 1.5 m thick. On the basis of outcrop distribution and drill-hole intersections, the Nutkwa Main and North deposits have strike lengths of 430 and 400 m, respectively, and are believed to represent the same stratigraphic horizon (Hattie and others, 1996). Pyrite and abundant fine-grained sphalerite are the dominant sulfides, together with minor chalcopyrite and sparse galena. A clastic texture is characteristic of the Nutkwa Main deposit, in which fragments of chlorite schist, sericite schist, and quartz occur within a pyrite- and sphalerite-rich matrix. The presence of as much as 1.8 weight percent Ba in drill cores at the Nutkwa North deposit (Hattie and others, 1996) suggests the

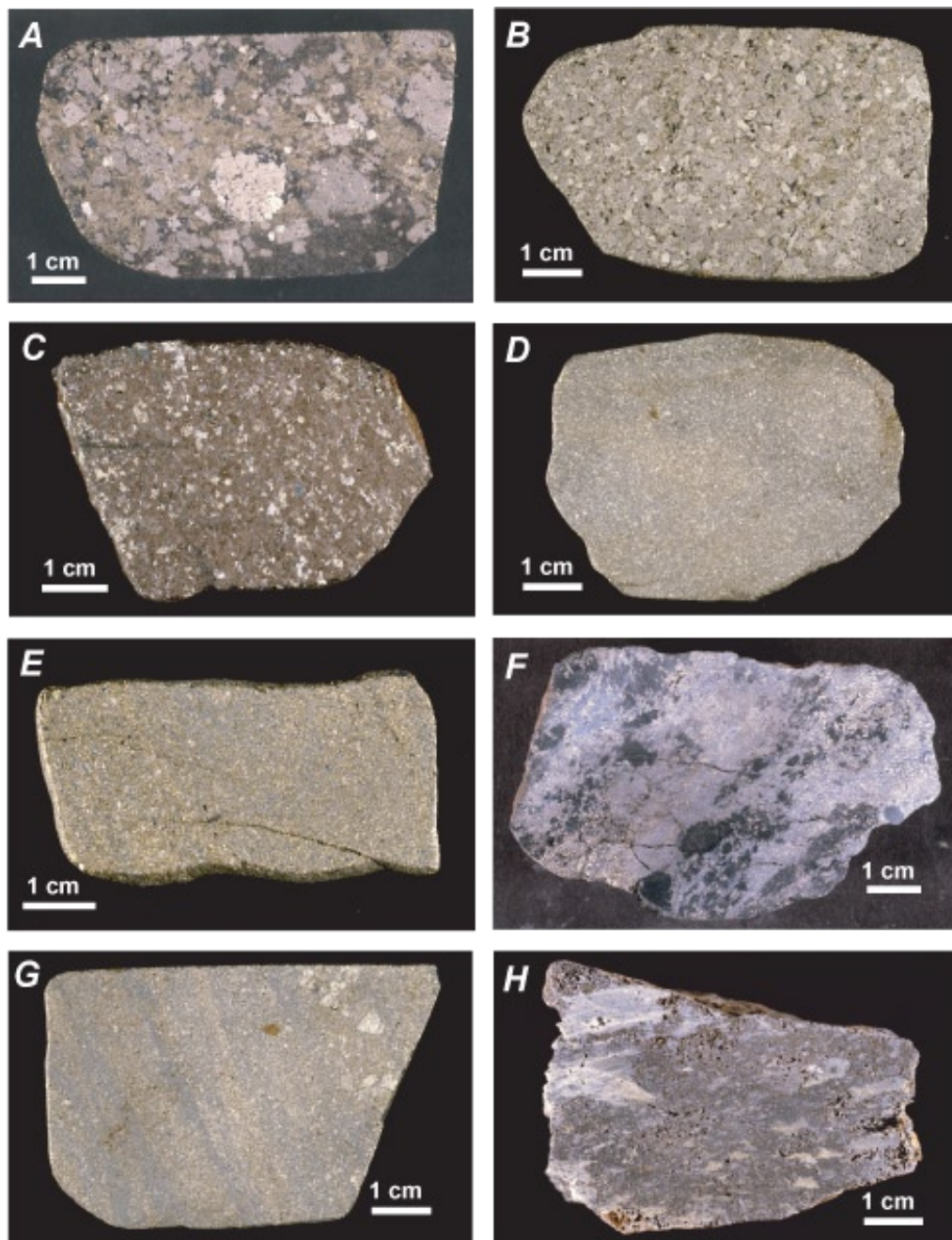


Figure 2. Representative sulfide-rich samples from volcanogenic massive sulfide deposits in study area (fig. 1). *A*, Very coarse grained porphyroblastic pyrite in a matrix of chalcopyrite, pyrrhotite (partially altered to marcasite), and minor sphalerite. Stumble-On Mine dump, sample JS-00-36A. *B*, Coarse-grained granoblastic pyrite within a matrix of fine-grained chalcopyrite and minor sphalerite. Khayyam Mine upper dump, sample JS-00-62A. *C*, Coarse-grained disseminated pyrite (minor) within a matrix of coarse-grained, granular sphalerite (abundant). Stumble-On Mine dump, sample JS-00-36C. *D*, Pyritic massive sulfide with minor interstitial sphalerite and trace chalcopyrite. Keete Inlet Mine dump, sample JS-00-53A. *E*, Massive chalcopyrite and sphalerite with minor pyrite. Copper City Mine dump, sample JS-00-55A. *F*, High-grade polymetallic massive sulfide with abundant sphalerite and galena, and minor chalcopyrite, and relict volcanic clasts (dark). Ruby Tuesday (Fish Show) Mine dump, sample RT-FS-MS. *G*, Layered pyrite, sphalerite, minor chalcopyrite, with local coarse-grained pyrite (right). Dama deposit, sample LO-53/624.2. *H*, Pyrite and sparse galena with sericite-rich rhyolite lapilli(?). Barrier Islands No. 2 occurrence, sample BI-2-MS.

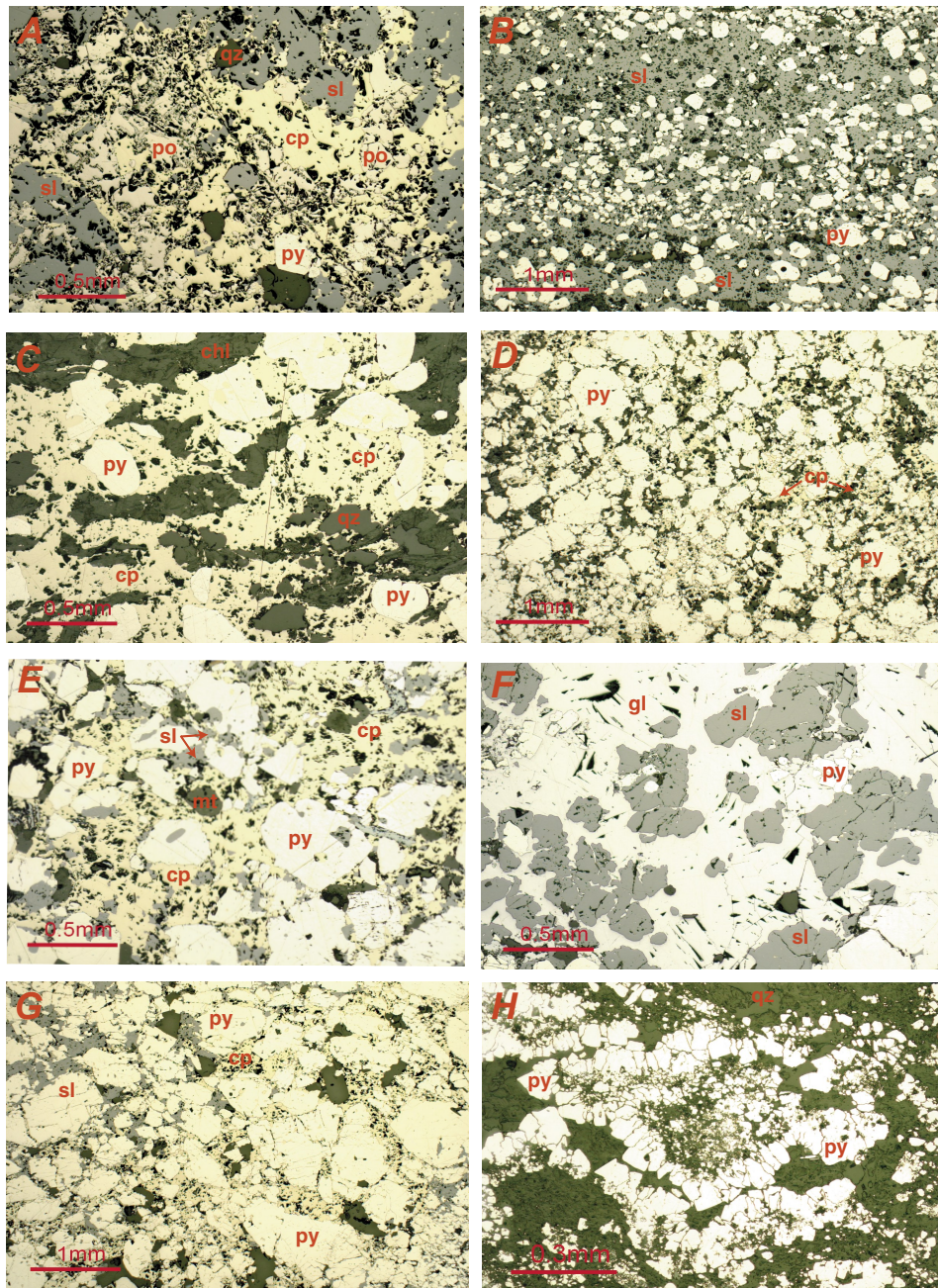


Figure 3. Photomicrographs (all in reflected light) of sulfide-rich samples from the study area (fig. 1). Minerals: chl, chlorite; cp, chalcopyrite; gl, galena; mt, magnetite; po, pyrrhotite; py, pyrite; qz, quartz; sl, sphalerite. *A*, Abundant pyrrhotite intergrown with chalcopyrite, sphalerite, and minor pyrite and quartz. Stumble-On Mine dump, sample JS-00-36D. *B*, Layers of sphalerite- and pyrite-rich massive sulfide. Corbin Mine dump, sample JS-00-56I. *C*, Chalcopyrite and coarse-grained pyrite within a matrix of foliated chlorite and quartz. Big Harbor West deposit, sample JS-00-31C. *D*, Coarse-grained pyrite within a matrix of fine-grained chalcopyrite, quartz, and minor sphalerite. Keete Inlet Mine dump, sample JS-00-53A. *E*, Coarse-grained pyrite within a matrix of chalcopyrite and minor sphalerite and magnetite. Copper City Mine dump, sample JS-00-55C. *F*, Intergrowths of sphalerite and galena with minor pyrite. Ruby Tuesday (Fish Show) deposit, sample RT-FS-MS. *G*, Granular pyrite within a matrix of fine-grained sphalerite, chalcopyrite, and quartz. Dama deposit, sample LO-53/624.2. *H*, Fine-grained anhedral and coarse-grained euhedral pyrite in quartz. Barrier Islands No. 2 occurrence, sample BI-2-MS.

presence of barite, although this element could also reside in Ba-rich feldspar and (or) mica. The deposit contains zones of abundant Mn oxides, as much as 1 m thick (Hattie and others, 1996).

The small Hozer deposit (HZ, fig. 1) occurs south of the Nutkwa deposits on the south side of Keete Inlet. Host rocks are mainly felsic schist, quartz-rich metatuff, and greenstone breccia, all of which are metamorphosed to lower-green-schist-facies assemblages. Sulfides consist of disseminated pyrite, minor sphalerite, and sparse chalcopyrite, together with stringers and veinlets of pyrite; no massive sulfide is known from the area (Maas and others, 1991). This mineralized sequence may be part of the same stratigraphic section that contains the Nutkwa deposits to the north.

Four small stratiform sulfide occurrences in the Wales Group probably represent exhalative VMS deposits. Such exhalites are believed to form by chemical precipitation of sulfide and other minerals from hydrothermal plumes distal from high-temperature sea-floor vent sources (for example, Spry and others, 2000). The Deer Bay exhalite (DB, fig. 1), on the west side of Hetta Inlet, consists of disseminated pyrite, minor chalcopyrite, and sparse sphalerite in a pyritic quartz-sericite-chlorite schist (Maas and others, 1995). To the northwest, the Cable Creek roadcut occurrence (CCR, fig. 1; Maas and others, 1995) contains disseminated to semi-massive pyrite with minor sphalerite and chalcopyrite; barren pyritic schist to the east, termed the "Trocadero Bay exhalite," is probably a lateral facies equivalent. A similar sulfide occurrence at Security Cove (SC, fig. 1), on the southwest side of Dall Island, consists of thin (<20 cm thick) layers of massive pyrite and locally abundant sphalerite and galena with sparse chalcopyrite; accessory barite is implied by the presence of as much as 2.3 weight percent Ba (Berg, 1984; Maas and others, 1995).

One stratabound barite deposit is known on the south end of the Lime Point peninsula (fig. 1). Although it lacks associated sulfide minerals, the Lime Point deposit (LP, fig. 1) is important metallogenically because it occurs in the same metavolcanic and metasedimentary sequence that hosts the Copper City ore body 8 km to the north (CC, fig. 1; Maas and others, 1995). The Lime Point deposit differs, however, in being localized within a unit of calcite marble and minor interbedded talc schist. Barite there consists of massive, essentially pure bodies, 3 to 12 m thick and ~30 m long, that are discordant to bedding in the host marble (Elmendorf, 1920; Fowler, 1948; Twenhofel and others, 1949). In outcrop and underground in the adit, the barite shows abundant evidence of an early, pre-tectonic replacement of the precursor limestone, including the presence of tightly folded barite lenses in marble. It is unknown, however, whether this barite formed mainly on the sea floor contemporaneously with carbonate sediment, as a broadly syndimentary (early diagenetic) replacement of limestone, like some stratabound barite deposits elsewhere (for example, Ketner, 1975; Ahsan and Mallick, 1999; Kelley and others, 2004), or as a late diagenetic replacement deep in the subsurface.

Deposits in the Moira Sound Unit and Correlatives

Several VMS deposits are known in the Niblack anchorage area (fig. 1; table 1). Massive sulfides and local stringer sulfides there occur in a sequence composed dominantly of felsic metavolcanic and tuffaceous metasedimentary rocks that traditionally have been assigned to the Wales Group (for example, Peek, 1975; Gehrels and Berg, 1992; Maas and others, 1995). These assignments are supported by a U-Pb zircon age of 595 ± 20 m.y. determined by Gehrels and others (1996) on a massive rhyolite at Lookout Mountain. This Late Proterozoic age is inconsistent, however, with various geologic data which suggest that the host rocks of these VMS deposits belong to the younger Moira Sound unit and not to the older Wales Group (see Karl and others, this volume).

The Niblack deposit (NL, fig. 1) consists of a series of irregular lenses of massive sulfide, as much as 9 m thick and 60 m long, within a host sequence of tuffaceous metarhyolite and minor interbedded clastic sedimentary rocks (Brooks, 1902; Wright and Wright, 1908; Herreid, 1964; Peek, 1975). Footwall rocks stratigraphically below the mineralized sequence comprise metadacite and metabasaltic greenstone; hanging-wall rocks above this sequence consist largely of metabasalt (Niblack Mining Corp., 2006, URL <http://www.niblackmining.com/>). Regional metamorphic grade is lower greenschist facies. The massive sulfides consist of pyrite and chalcopyrite, generally minor sphalerite, and sparse galena. Disseminated and stringer sulfides also occur nearby, the stringers probably representing part of a footwall feeder zone to the massive sulfides stratigraphically above. Related hydrothermal sedimentary rocks present in the mine area include jasper, magnetite iron-formation, metachert, and quartz-piemontite-spessartine (Peek, 1975; Adamson and Gray, 1995).

Several other significant VMS deposits occur in the Niblack area, the largest of which is the Lookout Mountain deposit (LO, fig. 1), about 1,300 m south-southeast of the Niblack Mine (NL, fig. 1). Host rocks to this deposit consist of a deformed sequence of pyritic rhyolite metatuff that locally contains sulfide-rich clasts; a Mn-rich piemontite-spessartine-rhodonite layer occurs in the stratigraphic hanging wall (Adamson and Gray, 1995). Footwall rocks are mainly metabasaltic amygdaloidal greenstone that in places displays relict pillow structures. The massive sulfides on Lookout Mountain form three stacked lenses separated by zones of disseminated and stringer sulfides with an aggregate thickness of about 60 m; individual massive sulfides lenses are as much as 14 m thick (Green, 2006; Niblack Mining Corp., 2006, URL <http://www.niblackmining.com/>). Comparable thicknesses of mineralized rock have been intersected in drilling at the nearby Dama (DM, fig. 1), Lindsay/88 (LS, fig. 1), and Trio/Broadgauge deposits (Adamson and Gray, 1995). In all of these deposits, pyrite is the chief sulfide mineral, accompanied by varying amounts of sphalerite and chalcopyrite with appreciable gold in places. The sulfides form massive zones and seams within strongly sericite altered rhyolite tuff or, less

commonly, alternating layers composed dominantly of pyrite and sphalerite (fig. 2*G*). Some samples show relatively coarse grained pyrite with interstitial sphalerite and chalcopyrite (figs. 2*G*, 3*G*).

The Moira Copper deposit (MC, fig. 1), also known as the Wakefield group of claims (Wright and Wright, 1908; Maas and others, 1995), occurs about 2 km west-northwest of the Niblack Mine (NL, fig. 1). This small VMS deposit forms a lens of sulfides, as much as 3 m thick, within a sequence of metabasaltic greenstone and metarhyolitic rocks that also includes interbedded volcanoclastic sedimentary rocks. Similar to the deposits in the Niblack area, the Moira Copper deposit is hosted in weakly deformed rocks that have been regionally metamorphosed to lower greenschist facies. The sulfide body consists of semimassive pyrite and chalcopyrite with trace sphalerite.

Small VMS deposits and occurrences are known in several places along the southwest and south ends of Prince of Wales Island (fig. 1). Dominantly volcanic and lesser sedimentary host rocks in these areas are correlated with the Moira Sound unit by Karl and others (this volume). Occurrences on the Barrier Islands are mainly within rhyolitic tuff and siliceous black slate and are surrounded by a sequence composed dominantly of pillow basalt and pyroclastic breccia (Gehrels and others, 1983); rhyolite domes are present locally. Thin stratiform lenses of barren semimassive to massive pyrite are common, associated with lenses of sericite schist (fig. 2*H*). Textures of the pyrite are distinctive and differ from those in all other VMS deposits of the region, in which aggregates of fine-grained anhedral pyrite and rare framboidal pyrite are intergrown with coarse-grained euhedral pyrite (fig. 3*H*). Some sulfide-rich samples include sparse sphalerite and chalcopyrite and traces of galena. One pyritic lens in black slate at the Barrier Islands No. 1 deposit (BI-1, fig. 1) contains >5,000 ppm Ba (Gehrels and others, 1983, table 1), probably in barite or Ba-rich mica.

VMS deposits and occurrences are also known in the Nichols Bay area (fig. 1), the largest of which, at the northeast end of the bay, is the Nichols Bay Shaft deposit (NB, fig. 1; Chapin, 1918; Gehrels and others, 1983; Maas and others, 1995). Host rocks consist of interbedded slate, graywacke, and siliceous volcanic rocks, including chert. This deposit is within the contact aureole of a large granitic pluton of Devonian or Silurian age (Gehrels, 1992; see Karl and others, this volume). Sulfides form lenses and layers, several centimeters thick, composed of pyrite, pyrrhotite, minor sphalerite and magnetite, and sparse chalcopyrite; garnet porphyroblasts also occur in the massive sulfide. Other VMS occurrences in the Nichols Bay area are small and consist chiefly of pyrite with trace sphalerite (Gehrels and others, 1983; Maas and others, 1995).

A small VMS occurrence on the southeast side of Dall Island at Datzkoo Harbor (DH, fig. 1) consists of thin (<10 cm thick) lenses within quartz-sericite phyllite of probable felsic volcanic or volcanoclastic origin, associated with hornblende schist, talc schist, and felsic schist (Maas and others, 1995). Metamorphic grade is upper greenschist or, possibly, lower amphibolite facies. The sulfide lenses are composed almost

wholly of coarse-grained pyrite with only sparse sphalerite and trace chalcopyrite. Accessory barite is suggested by the presence of 1.3 weight percent Ba in one sample analyzed by Maas and others (1995).

Bulk Geochemistry of Sulfide-Rich Samples

Sampling and Data Compilation

The limited number of samples collected during this study provides only a reconnaissance coverage of VMS deposits in the region. Although care was taken to obtain representative samples from mine dumps, adits, and drill cores, these samples do not necessarily reflect the true mineralogic and chemical variations in a given deposit, especially in mine dumps that were previously sampled—some extensively—by earlier workers. Moreover, before 1910 and the widespread use of froth-flotation technology for efficiently separating Zn from Cu and Pb in polymetallic ores, sphalerite commonly was not recovered; sphalerite also was a penalty in the ores during smelting. Thus, a disproportionate amount of this mineral may have been left on the mine dumps during early mining operations.

For compilation purposes here, geochemical data for base and precious metals acquired during this study are combined with those of Maas and others (1995, table A-2) and several exploration and mining company reports. The mining-company data were obtained in the 1980s and 1990s on a diverse suite of sulfide-rich samples from mine dumps, underground workings, and drill cores. Because of proprietary issues, these data are not individually cited here but, instead, are included with those of Maas and others (1995) and this study to permit calculation of more meaningful averages for Cu, Zn, Pb, Ag, and Au contents in the deposits under consideration.

Base and Precious Metals

Average base- and precious-metal contents in the major VMS deposits of the study area (fig. 1) are listed in table 2, and representative analyses of individual samples are listed in table 3 (Wales Group) and table 4 (Moira Sound unit). Overall, the sulfide-rich (>10 volume percent) samples contain proportionately much more Cu and Zn than Pb (fig. 4*A*). Elemental data in samples from the VMS deposits in the Wales Group deposits display a similar distribution to those from the Moira Sound unit, which are dominated by more Zn rich bulk compositions. We note, however, that this difference may be only an artifact of sampling density. The maximum average Pb content was measured in samples from the Ruby Tuesday (Fish Show) deposit (table 2). One relatively Pb rich sample from the Nutkwa North deposit (NKN, fig. 1), in the Wales

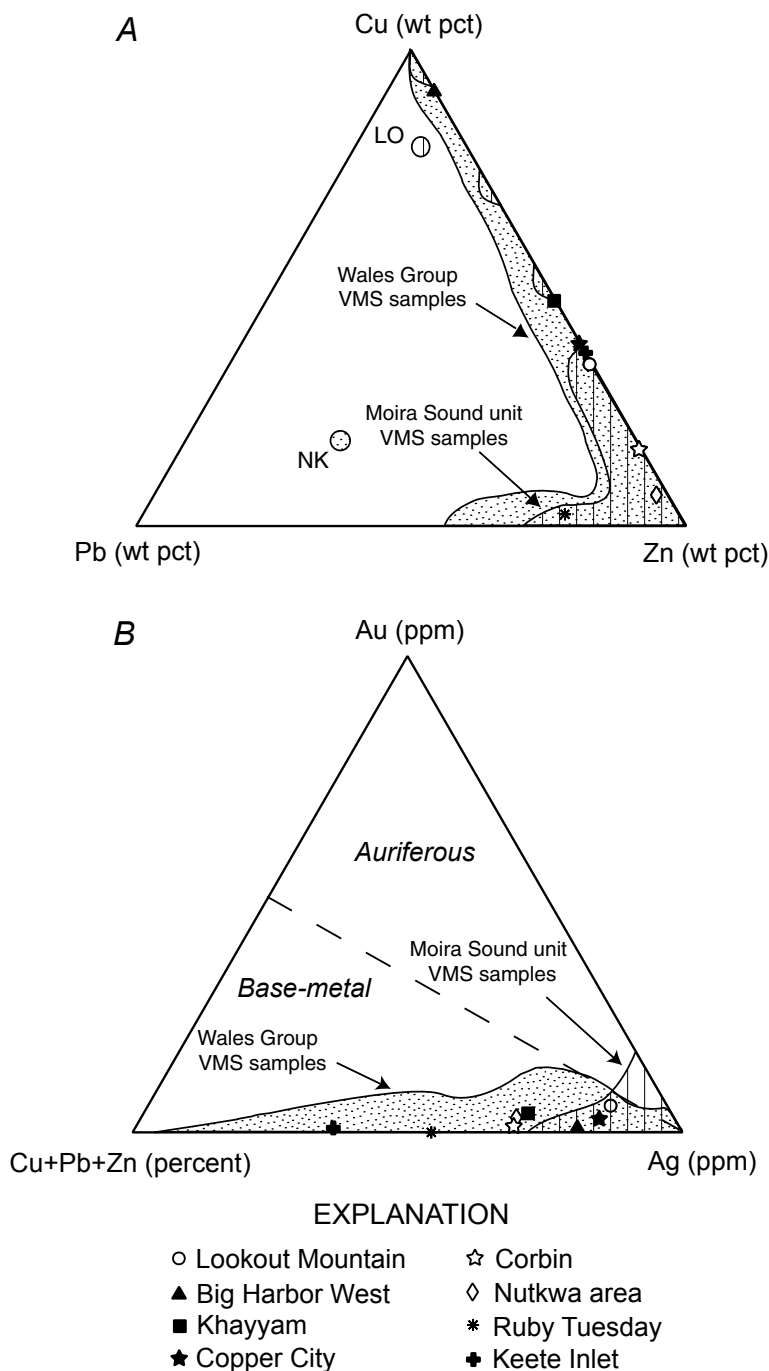


Figure 4. Ternary plots of average whole-rock compositions of sulfide-rich samples from significant volcanogenic massive sulfide (VMS) deposits in study area (fig. 1). Separate fields for samples from Wales Group deposits (stippled) and Moira Sound unit deposits (hatched) are compiled from data of Barrie (1984), Thurston (1994), Maas and others (1995), Terry and Gibson (1998), Abacus Mining and Exploration Corp. (2003, URL <http://www.amemining.com/>), and this study (tables 3, 4). A, Cu-Pb-Zn ternary plot. LO, Lookout Mountain (including the Dama deposit); NK, Nutkwa area. Data for two samples of base-metal-poor massive pyrite from the Barrier Islands are omitted. B, (Cu+Pb+Zn)-Au-Ag ternary plot. Auriferous and base-metal fields for ancient VMS deposits ($n=370$) from Hannington and others (1999).

Table 2. Average base- and precious-metal contents in sulfide-rich samples from major volcanogenic massive sulfide deposits on southern Prince of Wales Island, southeastern Alaska.

[Data are compiled only for mineralized samples containing >3 weight percent Cu+Pb+Zn; data sources: Barrie (1984), Thurston (1994), Maas and others (1995), Terry and Gibson (1998), and this study]

Deposit (fig. 1)	<i>n</i>	Cu (wt pct)	Pb (wt pct)	Zn (wt pct)	Ag (ppm)	Au (ppm)
Khayyam -----	29	4.86	<0.01	5.16	27.2	1.65
Big Harbor West -----	12	11.7	0.04	1.07	56.9	0.85
Ruby Tuesday ¹ -----	5	0.52	4.44	16.4	25.6	0.11
Copper City -----	7	9.52	0.08	15.3	155	5.70
Corbin -----	14	2.69	0.09	14.0	38.8	0.87
Keete Inlet -----	4	2.36	<0.01	4.13	8.8	0.29
Nutkwa ² -----	25	1.29	0.42	18.1	47.7	2.33
Lookout Mountain ³ -----	--	1.70	⁴ 0.03	3.22	36.4	2.77

¹Includes both the Fish Show and Polymetal Lode deposits.

²Includes both the Nutkwa Main and Nutkwa North deposits.

³Inferred geologic resource from Niblack Mining Corp. (2006, URL <http://www.niblackmining.com/>).

⁴Estimated from analyses of four U.S. Geological Survey samples.

Group, is compositionally distinct from the other samples (fig. 4A), probably because of its very low base-metal contents.

Average proportions of base and precious metals in major VMS deposits of the study area (fig. 1), including the fields defined by individual samples from the VMS deposits in the Wales Group and Moira Sound unit, are plotted in figure 4B. In contrast to the pattern shown by base metals only (fig. 4A), figure 4B suggests that the samples from the Moira Sound unit are slightly Ag rich relative to those from the Wales Group. Sulfide-rich samples from the Wales Group generally contain proportionately more Cu+Pb+Zn and less Ag relative to those from the Moira Sound unit. We do not consider this difference to be an artifact of sampling density because the Ag-poor compositions of samples from the Wales Group are distinct from those of samples from the Moira Sound unit. Au proportions are broadly similar in both sample groups. We note, however, that the Au proportions in individual samples vary considerably, with the maximum values occurring in samples from the Copper City, Lookout Mountain, and Nutkwa deposits (table 2), possibly reflecting isolated gold grains in single samples rather than a homogeneous distribution of Au.

Trace Metals

Bulk compositions of sulfide-rich rocks vary widely for many metals. Among the trace metals, Co content ranges from <10 to 398 ppm and broadly correlates with Ni content (<10–253 ppm); maximum contents of both Co and Ni occur mostly in samples from the Khayyam and Stumble-On deposits (fig. 5A). Samples containing more than 1 weight percent Cu show an overall positive correlation of Cu with Ag

contents; maximum Ag contents were measured in samples from the Copper City and Niblack-Lookout Mountain deposits (fig. 5B). A positive correlation between Pb and Sb in some samples (fig. 5C) suggests the presence of one or more Pb-Sb sulfosalts minerals, such as boulangerite (Pb₅Sb₄S₁₁) or bournonite (PbCuSbS₃), particularly in galena-rich samples from the Ruby Tuesday (Fish Show) deposit. Somewhat high contents of Sb (max 77 ppm) and Ag (max 310 ppm) may reflect, respectively, Sb-rich pyrite in one sample from the Barrier Islands No. 2 deposit and minor tetrahedrite [(Cu,Fe,Ag)₁₂(Sb,As)₄S₁₃] in one sample from the Copper City deposit (fig. 5D). Overall, Zn and Hg contents show a positive correlation, with samples from the Khayyam and Stumble-On deposits yielding the maximum Hg content for a given Zn content (fig. 5E). Au and As contents are uncorrelated, even for Au-rich (4.4–9.3 ppm) samples from the Copper City, Khayyam, Lookout Mountain, and Niblack deposits (fig. 5F).

Sulfide Mineral Chemistry

LA-ICP-MS analyses of different sulfide minerals show a range of nonessential-element contents that reflects both mineral inclusions and crystallographic substitutions (for example, Huston and others, 1995), where “nonessential elements” are defined as metals and nonmetals that are not required for the formation of a specific sulfide mineral, such as Cu and Pb in pyrite and Sb and Ag in galena. Mineral inclusions containing nonessential elements are easily observed microscopically in reflected light, although some are too small (<1 μm diam) to be visible even at 500× magnification. The

Table 3. Representative whole-rock analyses of sulfide-rich samples from volcanogenic massive sulfide deposits in the Wales Group on southern Prince of Wales Island and vicinity, southeastern Alaska.

[Major-element analyses in weight percent; minor- and trace-element analyses in parts per million. All analyses were performed at XRAL Laboratories in Denver, Colo., by inductively coupled plasma atomic-emission spectrometry, atomic-absorption spectrometry, and fire-assay methods. Total Fe as Fe₂O₃. Elements analyzed for but not measured above their lower limits of detection (in parentheses): Be (1 ppm), U (100 ppm)]

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Major elements															
Al ₂ O ₃	0.18	0.72	0.12	0.24	0.13	6.40	5.45	3.66	0.35	0.43	0.12	1.27	2.71	5.53	8.65
TiO ₂	<0.01	0.04	0.01	<0.01	<0.01	0.03	0.03	0.13	<0.01	<0.01	<0.1	0.01	0.02	0.09	0.10
Fe ₂ O ₃	43.6	41.3	37.2	15.2	43.9	29.0	31.0	16.0	33.6	43.8	23.0	40.0	29.0	45.5	11.6
MnO	0.006	0.012	0.002	0.029	0.005	0.137	0.284	0.019	0.063	0.016	0.023	0.556	0.025	0.008	0.007
MgO	0.09	0.36	0.06	0.22	0.09	3.83	5.78	0.02	0.08	0.42	0.09	1.28	0.58	1.25	0.72
CaO	0.08	0.04	0.08	0.03	0.03	0.13	0.27	0.01	0.26	0.03	0.11	2.11	0.03	0.03	0.13
Na ₂ O	<0.01	<0.01	0.01	0.01	<0.01	0.04	<0.01	0.25	0.01	<0.01	<0.01	<0.01	0.12	0.26	0.15
K ₂ O	<0.01	0.01	<0.01	<0.01	0.01	0.06	0.11	2.41	<0.01	<0.01	<0.01	<0.01	0.64	1.34	2.71
P ₂ O ₅	0.03	0.03	0.01	0.02	0.02	0.09	0.17	0.01	0.16	0.03	0.02	0.04	0.03	0.03	0.04
S	50.4	43.6	34.7	34.3	37.0	18.9	26.6	27.1	41.2	42.1	36.9	37.4	38.0	41.8	9.04
Minor and trace elements															
Li	<2	<2	<2	<2	<2	20	16	<2	<2	<2	<2	<2	<2	<2	3
Sr	<2	<2	<2	<2	<2	5	3	7	15	<2	109	130	50	7	8
Ga	48	40	30	121	48	63	38	25	60	39	76	50	39	39	19
V	74	86	27	67	85	96	19	16	24	34	15	158	44	90	39
Sc	<2	<2	2	<2	<2	<2	<2	3	<2	<2	<2	<2	<2	4	4
Co	78	146	19	45	112	39	16	4	19	157	40	24	19	182	61
Ni	14	16	11	4	42	8	7	14	15	15	7	12	12	37	5
Mo	26	56	8	14	26	20	8	111	46	46	27	24	45	18	39
Cu	13,910	63,850	342,000	386	18,950	45,160	233,700	700	69,780	107,800	588	13,830	3,270	298	15,210
Pb	19	41	50	12	8	37	620	63,440	205	205	5,600	69	4,630	30	16
Zn	30,530	113,100	19,140	566,700	124,100	490	2,840	248,300	251,200	2,420	426,100	71,340	297,500	804	238
Cd	72	269	80	2,160	422	<2	13	806	763	4	1,600	173	909	<2	<2
Bi	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	95	<50	<50	<50	<50
Ag	9	35	136	4	22	17	97	62	127	70	81	7	19	<2	31
Au	0.60	1.65	1.37	0.09	0.10	1.08	1.49	0.15	5.38	1.48	0.30	0.41	0.09	<0.01	0.17
Sb	<0.60	<0.60	<0.60	0.70	<0.60	2.00	1.00	56.2	10.8	11.0	3.80	<0.60	4.30	<0.60	<0.60
As	64.1	59.0	6.50	4.70	37.9	41.8	11.8	250	21.2	591	11.0	12.2	6.30	5.70	12.0
Se	11.5	39.3	<0.20	1.50	4.50	4.60	3.50	13.3	0.20	168	6.30	1.70	1.10	16.4	15.3
Te	2.30	53.8	<0.10	0.40	2.30	8.10	0.40	5.90	5.70	37.7	36.3	1.00	0.10	6.70	5.80
Hg	0.38	1.14	0.40	8.71	1.94	0.14	0.56	8.46	15.9	1.2	31.3	1.17	14.0	0.08	0.14
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	2.1	<0.1	0.2	0.6	<0.1	0.2

Samples:

1. JS-00-33H, upper Khayyam Mine dump; granoblastic pyritic sulfide with minor matrix chalcopyrite and sphalerite.
2. JS-00-62E, lower Khayyam Mine dump; granoblastic pyritic sulfide with abundant matrix sphalerite and chalcopyrite.
3. JS-00-62F, lower Khayyam Mine dump; massive fine-grained chalcopyrite with sparse sphalerite and quartz.
4. JS-00-36C, Stumble-On Mine dump; granoblastic sphalerite with minor pyrite.
5. JS-00-36D, Stumble-On Mine dump; massive fine-grained pyrrhotite with sphalerite and minor pyrite.
6. JS-00-29C, Big Harbor East Mine adit; semimassive pyritic sulfide in quartz-chlorite schist with abundant chalcopyrite.
7. JS-00-31D, Big Harbor West Mine outcrop; semimassive chalcopyrite in chlorite schist with minor pyrite and sparse sphalerite.
8. RT-FS-MS, Ruby Tuesday (Fish Show) Mine dump; semimassive sphalerite in felsic tuff with abundant galena and sparse chalcopyrite.
9. JS-00-55C, Copper City Mine dump; massive fine-grained chalcopyrite with abundant pyrite and minor chalcopyrite and quartz.
10. JS-00-56D, Corbin Mine dump; massive fine-grained pyritic sulfide with abundant chalcopyrite and trace sphalerite.
11. JS-00-56J, Corbin Mine dump; layered massive sphalerite and pyrite with sparse quartz and trace galena.
12. JS-00-53D, Keete Inlet Mine dump; massive pyritic sulfide with minor chalcopyrite, sphalerite, quartz, magnetite, and carbonate.
13. JS-00-39A, Nutkwa Mine dump; massive pyritic sulfide with abundant sphalerite, minor quartz, chlorite, and sericite, and sparse chalcopyrite and galena.
14. JS-00-42A, Trocadero Bay "exhalite" outcrop; coarse-grained pyritic sulfide with minor quartz, sericite, and chlorite and trace chalcopyrite and sphalerite.
15. JS-00-66, Deer Bay "exhalite" outcrop; quartz-sericite-chlorite schist with disseminated pyrite and sparse chalcopyrite.

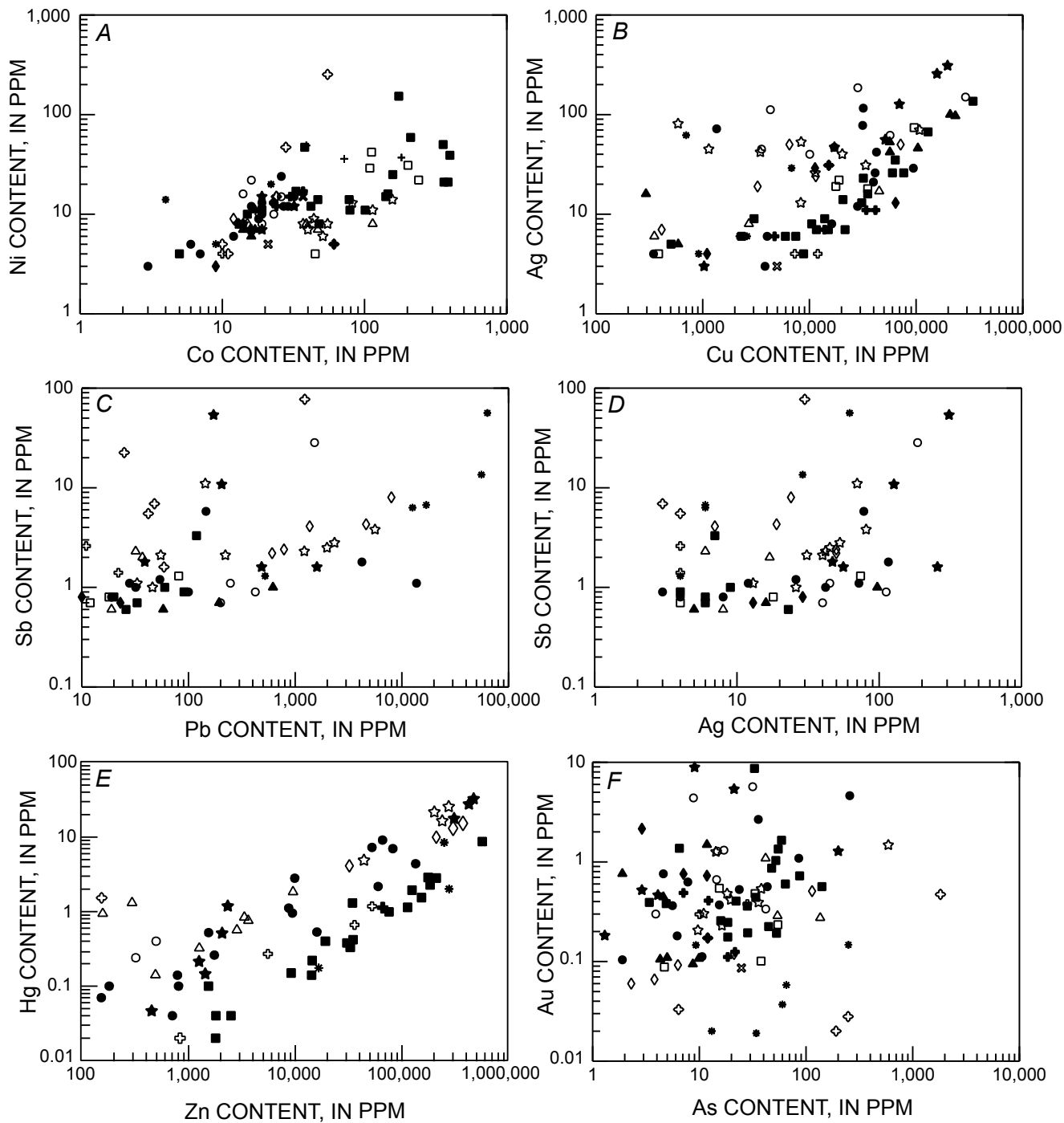
Table 4. Representative whole-rock analyses of sulfide-rich samples from volcanogenic massive sulfide deposits in the Moira Sound unit on southern Prince of Wales Island and vicinity, southeastern Alaska.

[Major-element analyses in weight percent; minor- and trace-element analyses in parts per million. All analyses were performed at XRAL Laboratories in Denver, Colo., by inductively coupled plasma atomic-emission spectrometry, atomic-absorption spectrometry, and fire-assay methods. Total Fe as Fe₂O₃. Elements analyzed for but not measured above their lower limits of detection (in parentheses): Be (1 ppm), U (100 ppm)]

Sample -----	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Major elements															
Al ₂ O ₃ ----	0.48	4.77	4.79	0.23	0.29	2.11	5.88	1.87	3.53	5.87	1.33	14.3	3.14	0.93	6.38
TiO ₂ -----	<0.008	0.045	0.008	<0.008	<0.008	<0.008	0.008	0.018	0.017	0.025	0.13	0.42	0.08	0.04	0.04
Fe ₂ O ₃ ----	44.3	26.9	39.9	46.2	40.3	34.0	39.5	43.5	40.5	35.6	47.8	30.3	47.3	51.9	37.3
MnO -----	0.019	0.002	0.065	0.048	0.011	0.080	0.081	0.004	0.052	0.003	0.006	0.032	0.094	18.40	0.048
MgO -----	0.35	0.26	3.56	0.29	0.24	1.28	4.91	0.14	2.29	0.11	0.64	0.99	2.38	0.81	3.73
CaO -----	0.04	0.02	0.27	1.10	0.20	1.99	0.04	0.03	0.01	0.01	0.14	0.22	0.03	0.52	0.07
Na ₂ O -----	0.01	0.03	0.01	0.02	<0.01	<0.01	<0.01	0.61	0.09	0.20	0.03	0.27	0.02	<0.01	0.11
K ₂ O -----	<0.01	1.64	<0.01	<0.01	<0.01	<0.01	<0.01	0.25	0.13	1.63	0.19	4.06	0.17	0.01	0.92
P ₂ O ₅ -----	0.02	0.02	0.19	0.11	0.03	0.01	0.03	0.02	0.01	<0.01	0.01	0.01	0.01	0.06	0.04
S -----	41.9	23.8	34.5	18.1	45.5	32.1	33.7	44.2	29.9	26.4	37.5	23.0	35.2	23.3	33.0
Minor and trace elements															
Li -----	<2	<2	7	<2	<2	<2	8	<2	12	<2	9	10	5	3	11
Sr -----	<2	4	4	16	3	22	<2	10	5	17	4	17	<2	8	9
Ga -----	40	24	41	124	65	37	40	40	6	13	<4	13	8	<4	32
V -----	33	16	31	74	39	77	68	34	12	13	26	260	54	22	26
Sc -----	<2	2	2	<2	<2	4	3	<2	<2	6	<2	37	2	<2	<2
Co -----	26	12	29	19	23	19	26	23	55	22	55	28	102	11	37
Ni -----	24	6	12	13	10	8	15	13	<3	<3	253	47	<3	4	15
Mo -----	16	40	105	36	44	104	88	9	146	16	58	13	13	6	12
Cu -----	31,540	16,200	42,530	31,990	57,010	290,700	17,130	4,310	1,100	11,310	45	71	12	63	207
Pb -----	146	19	32	4220	29	35	20	423	12	10	25	1,230	22	42	10
Zn -----	9,870	152	8,660	65,750	134,400	1,740	15,930	785	496	30	56	153	143	6,390	898
Cd -----	51	<2	18	170	493	10	62	<2	3	<2	<2	<2	<2	55	<2
Bi -----	<50	<50	51	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Ag -----	78	8	42	116	62	150	47	112	4	29	<2	30	<2	4	<2
Au -----	4.62	0.53	1.09	11.0	0.66	0.30	0.34	4.39	0.76	2.15	0.03	0.47	0.03	0.01	<0.01
Sb -----	5.80	0.80	1.00	1.80	<0.60	<0.60	<0.60	0.90	<0.60	0.80	23	77	<0.60	5.50	<0.60
As -----	257	23.7	85.5	94.2	14.5	3.90	41.9	8.80	7.10	2.90	248	1,820	6.40	92.9	62.3
Se -----	3.90	2.10	19.0	0.40	1.10	0.40	4.70	5.20	19.5	4.00	3.40	<0.20	8.80	3.00	24.5
Te -----	29.7	9.60	66.2	50.0	22.2	<0.10	18.5	59.6	9.00	49.6	<0.10	0.10	5.80	2.20	7.80
Hg -----	2.81	0.07	1.12	9.11	4.39	0.26	0.53	0.14	0.40	0.84	0.07	1.53	0.09	0.09	0.05
Tl -----	0.3	0.2	<0.1	<0.1	<0.1	<0.1	0.1	0.2	<0.1	0.2	0.6	72	0.3	<0.1	0.2

Samples:

1. JS-00-28A, lower Niblack Mine dump; weakly layered massive pyritic sulfide with minor chalcopyrite and sparse sphalerite.
2. JS-00-28C, lower Niblack Mine dump; siliceous rocks with abundant disseminated pyrite, lesser chalcopyrite, and minor sericite.
3. JS-00-28L, upper Niblack Mine dump; semimassive pyrite and chalcopyrite in quartz-bearing chlorite schist.
4. 84AGK053C, upper Niblack Mine dump; massive magnetite iron-formation with abundant pyrite and chalcopyrite and angular clasts of jasper.
5. LO-53/624.2, Dama Prospect drill core, Niblack area; layered pyrite, sphalerite, and minor chalcopyrite.
6. LO-61/573.0, Dama Prospect drill core, Niblack area; massive fine-grained chalcopyrite with minor pyrite and sparse sphalerite.
7. LO-61/577.5, Dama Prospect drill core, Niblack area; semimassive pyritic sulfide in chloritic tuff(?) with sparse chalcopyrite and sphalerite.
8. LO-99/367, Lookout Mountain Prospect drill core, Niblack area; massive pyritic sulfide with minor quartz and sericite and trace chalcopyrite and sphalerite.
9. MC-MS-2, Moira Copper Mine dump; semimassive pyritic sulfide with abundant quartz, minor chlorite, and trace chalcopyrite.
10. MC-MS2, Moira Copper Mine dump; semimassive pyritic sulfide with minor quartz, chlorite, and sericite and sparse chalcopyrite.
11. B11-MS, Barrier Islands Prospect No. 1; brecciated massive fine-grained pyrite with sparse quartz and chlorite.
12. B12-MS, Barrier Islands Prospect No. 2; semimassive pyritic sulfide with abundant sericite and sparse quartz.
13. B17-MS, Barrier Islands Prospect No. 7; semimassive pyritic sulfide with minor quartz and chlorite.
14. B19-MS-1, Nichols Bay Mine dump; massive fine-grained pyrrhotite (partially oxidized) with abundant disseminated Mn-rich garnet, minor pyrite, and sparse sphalerite.
15. JS-00-57A, Datkoo Harbor occurrence, southeastern Dall Island; massive pyritic sulfide with minor quartz and chlorite and trace sphalerite.



EXPLANATION

- | | | |
|-----------------------------------|----------------|------------------|
| ● Niblack | ■ Khayyam | ⊕ Keete Inlet |
| ○ Lookout Mountain | □ Stumble-On | ⊕ Hozer |
| ◆ Moira Copper | ★ Copper City | ⊗ Datzkoo Harbor |
| ◇ Barrier Islands and Nichols Bay | ☆ Corbin | ⊗ Cable Creek |
| ▲ Big Harbor West | ◇ Nutkwa area | ◆ Deer Bay |
| △ Big Harbor East | * Ruby Tuesday | + Trocadero Bay |

Figure 5. Binary plots of whole-rock compositions of sulfide-rich samples from study area (fig. 1). *A*, Co versus Ni contents. *B*, Cu versus Ag contents. *C*, Pb versus Sb contents. *D*, Ag versus Sb contents. *E*, Zn versus Hg contents. *F*, As versus Au contents. Lookout Mountain includes the Dama deposit.

very high nonessential-element contents determined from some LA-ICP-MS spectra of apparently inclusion free spots probably record the presence of mineral inclusions on the surface of the sample that were too small to be easily visible, or were intersected by the laser beam during penetration as much as 10 μm below the surface. In our study, very large spectral peaks for nonessential elements (for example, Bi in pyrite, Sn in chalcopyrite) were screened during data reduction of the LA-ICP-MS analyses, such that the high contents of these elements were excluded from the calculated compositions. In some samples, such as those from the Big Harbor and Copper City deposits, meaningful analyses of sphalerite were unobtainable, owing to myriad small inclusions of chalcopyrite and (or) pyrite.

Pyrite

High nonessential-element contents in pyrite are dominated by Cu, Zn, and Pb contents that correlate with inclusions of chalcopyrite, sphalerite, and galena, respectively. Absolute abundances of these elements are unknown but estimated to range from several thousand parts per million to as much as several weight percent. Excluding base metals and trace elements that are unlikely to substitute for Fe within the pyrite lattice, the largest LA-ICP-MS spectral peaks are dominated by Mo, which likely reflects inclusions of molybdenite, although possible stoichiometric substitution of Mo for Fe cannot be ruled out (see Huston and others, 1995). High Mo contents were measured in pyrite grains from the VMS deposits in both the Wales Group (Corbin, Keete Inlet, Nutkwa Main) and the Moira Sound unit (Copper City, Dama). Some pyrite grains from the Corbin deposit also have high Bi, As, and Sb contents in the same analytical spots, suggesting residence in one or more sulfosalt minerals. Very high Bi contents unaccompanied by high Cu, Zn, Pb, As, or Sb contents in several pyrite grains from the Lookout Mountain and Niblack deposits may reflect the presence of native bismuth, which occurs in massive sulfide deposits elsewhere (for example, Craig, 1980; Callaghan, 2001). The high Sn content in some pyrite samples from the Moira Copper deposit suggests a host in either cassiterite or stannite. Detailed microbeam studies involving scanning electron microscopy and electron-microprobe analysis will be required to identify the mineralogic residence of these high metal contents.

Analyses of inclusion-free spots in pyrite ($n=170$) indicate mostly low contents of such elements as Co, Ni, Mn, Tl, As, Sb, and Se (figs. 6A, 6B; tables 5, 6), any of which may replace Fe (Co, Ni, Mn, Tl) or S (As, Sb, Se) within the pyrite lattice by either stoichiometric or nonstoichiometric substitution (Huston and others, 1995). With few exceptions, maximum contents are 200 ppm As, 30 ppm Sb, 200 ppm Co, 150 ppm Ni, 100 ppm Mn, 200 ppm Se, and 1 ppm Tl. As contents are relatively high in some pyrite samples from the Big Harbor East deposit (max 1,848 ppm) and the Ruby Tuesday (Fish Show) deposit (max 3,050 ppm), suggesting the presence of an $\text{Fe}(\text{As},\text{S})_2$ solid solution, as discussed for pyrite samples from other VMS deposits by Huston and others (1995). Pyrite

samples from the Khayyam and Stumble-On deposits are Co rich (max 1,436 and 2,057 ppm, respectively). Pyrite samples from the Barrier Islands deposits are distinctive in their extremely high contents of several trace elements, including maximum contents of 1.44 weight percent As, 283 ppm Sb, 3,552 ppm Mn, and 274 ppm Tl (figs. 6A, 6B; table 6). Pyrite from the Barrier Islands No. 2 deposit has the highest contents of these elements among the three localities sampled. Overall, pyrite samples from the Barrier Islands VMS deposits are chemically unlike those from other VMS deposits in the study area (fig. 1), suggesting different conditions of formation or preservation. The very high As, Sb, Mn, and Tl contents in pyrite samples from the Barrier Islands deposits do not require separate mineralogic residence but, instead, probably reflect substitution by these elements within the pyrite lattice (see Huston and others, 1995).

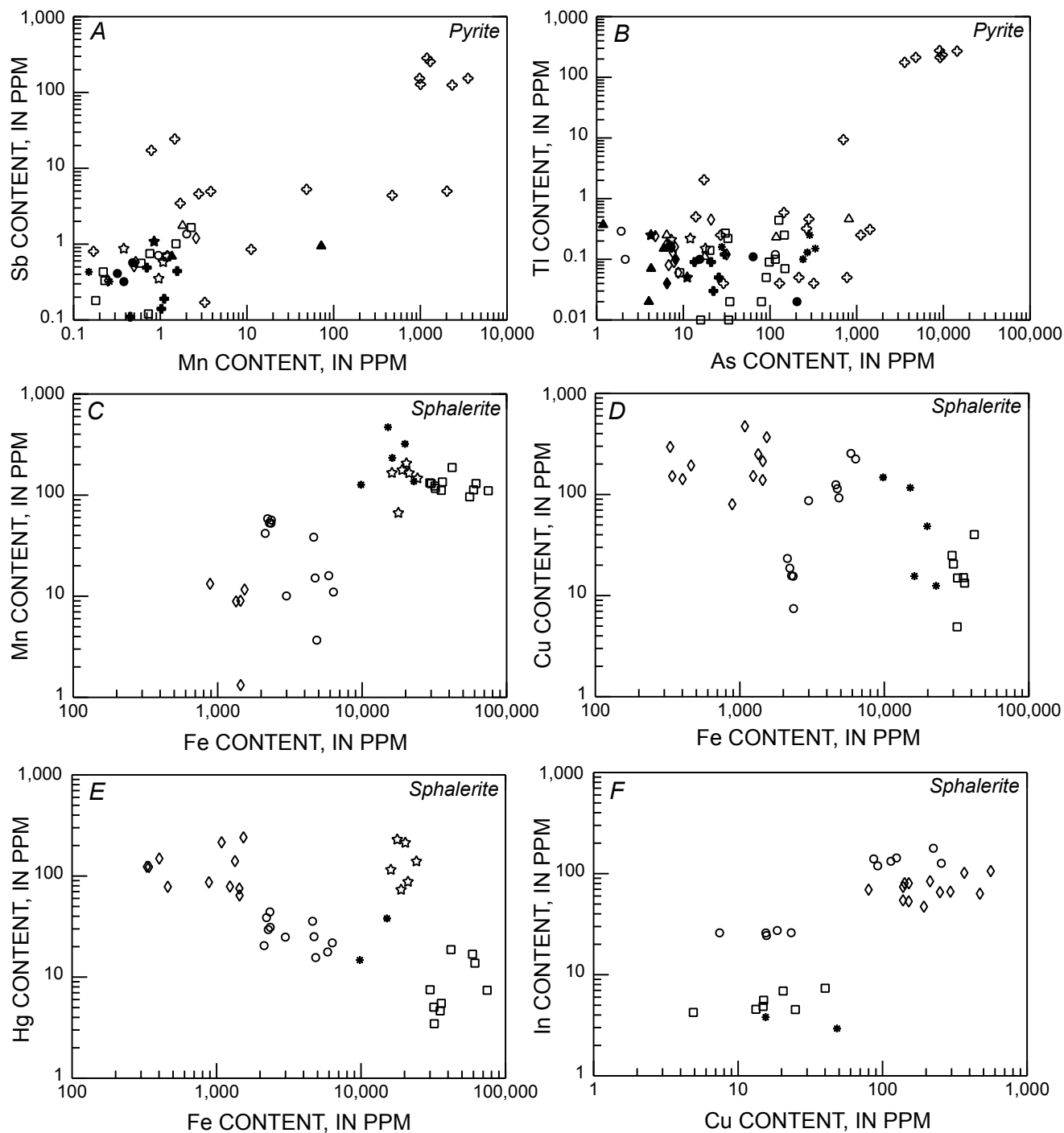
Pyrrhotite

Six analyses of inclusion-free pyrrhotite in a sample of massive coarse-grained pyrrhotite-pyrite-chalcopyrite ore from the Stumble-On Mine generally indicate low contents (<30 ppm) of a broad suite of trace elements (table 5), except for maximum contents of 86.6 ppm Ni and 1,147 ppm Se, which were measured in different analytical spots. Ni can substitute for Fe within the pyrrhotite lattice; however, it is unclear whether the high Se content reflects crystallographic substitution (that is, of Se for S) or the presence of a small Se-rich mineral inclusion.

Sphalerite

In hand specimens, sphalerite in the VMS deposits of the study area (fig. 1) varies widely in color, ranging from yellow at the Niblack area and Nutkwa deposits to black at the Khayyam and Stumble-On deposits. Sphalerite in all of these deposits is unzoned, as observed in polished and doubly polished thin sections. Some deposits (for example, Corbin, Khayyam, Ruby Tuesday) contain sphalerite with abundant small chalcopyrite inclusions. Galena inclusions are also common in sphalerite grains from the Corbin, Dama, Lookout Mountain, and Ruby Tuesday (Fish Show) deposits. During data reduction, large spectral peaks for Hg were identified in some sphalerite grains from the Khayyam deposit, and large peaks for In were measured in some sphalerite grains from the Dama and Nutkwa Main deposits, but because the size of these peaks implied contamination by inclusions (for example In in chalcopyrite), elemental contents were not determined.

Analyses of inclusion-free spots in sphalerite ($n=35$) show the presence of various trace elements (tables 7, 8) with generally dispersed patterns (figs. 6C-6F). These elements substitute for either Zn or S within the sphalerite lattice (for example, Huston and others, 1995). Overall, Fe contents range from 330 ppm in the Nutkwa Main deposit to 7.46 weight percent in the Khayyam deposit. Mn contents are relatively



EXPLANATION

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|-----------------------------------|--------------------------|----------------|
| ● Niblack | ▲ Big Harbor West | ☆ Corbin |
| ○ Lookout Mountain | △ Big Harbor East | ⊕ Keete Inlet |
| ◆ Moira Copper | □ Khayyam and Stumble-On | ◇ Nutkwa area |
| ◇ Barrier Islands and Nichols Bay | ★ Copper City | * Ruby Tuesday |

Figure 6. Binary plots of laser-ablation inductively coupled plasma mass-spectrometric analyses of sulfide-rich samples from study area (fig. 1). A, Mn versus Sb contents in pyrite. B, As versus TI contents in pyrite. C, Fe versus Mn contents in sphalerite. D, Fe versus Cu contents in sphalerite. E, Fe versus Hg contents in sphalerite. F, Cu versus In contents in sphalerite. Lookout Mountain includes the Dama deposit.

Table 5. Representative minor- and trace-element analyses of pyrite and pyrrhotite in sulfide-rich samples from southern Prince of Wales Island and vicinity, southeastern Alaska.

[Laser-ablation inductively coupled plasma mass-spectrometric analyses at the USGS laboratory in Denver, Colo. N.r., not reported. Minerals: po, pyrrhotite; py, pyrite. All samples contain minor to major amounts of quartz, and some also contain a minor amount of sericite. Fe content not reported]

Sample ---- Mineral-----	1 py	2 py	3 py	4 py	5 py	6 py	7 py	8 py	9 py	10 py	11 py	12 py	13 py	14 po	15 po
Mn -----	2.90	2.02	<0.01	3,550	<0.01	<0.01	<0.01	0.29	<0.01	0.85	0.38	1.03	<0.01	4.08	<0.01
Cu -----	1.52	8.66	8.57	56.4	9.64	n.r.	4.01	2.90	<0.01	n.r.	n.r.	1.58	3.65	n.r.	n.r.
Pb -----	0.02	0.27	<0.01	3.23	<0.01	<0.01	0.07	3.20	0.31	<0.01	<0.01	0.22	<0.01	<0.01	<0.01
Zn -----	3.22	<0.01	18.1	58.7	<0.01	12.5	5.40	7.66	0.85	8.30	8.61	6.29	18.3	21.9	<0.01
Sn -----	<0.01	<0.01	<0.01	1.25	3.87	1.01	1.49	2.30	0.44	1.59	2.77	<0.01	<0.01	12.8	1.90
Co -----	1.25	152	8.34	62.1	698	3.46	2,060	104	9.37	0.96	37.7	96.5	1.67	<0.01	2.75
Ni -----	12.4	4,600	131	32.3	6.65	271	1.22	55.4	79.4	35.0	22.2	29.5	5.00	6.37	25.2
Mo -----	1.10	3.18	<0.01	2.40	<0.01	2.16	0.15	<0.01	0.78	<0.01	0.42	1.25	<0.01	<0.01	<0.01
In -----	0.05	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	0.74	0.11	0.10	0.13	0.14	<0.01	0.36	<0.01
Cd -----	2.60	<0.01	1.42	<0.01	<0.01	<0.01	<0.01	3.82	3.91	0.51	<0.01	0.68	2.07	6.94	29.4
Bi -----	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.15	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ag -----	<0.01	2.29	2.01	4.67	<0.01	<0.01	1.02	<0.01	<0.01	0.09	0.62	2.02	0.69	22.9	3.31
Sb -----	<0.01	1.36	<0.01	154	0.31	1.01	<0.01	<0.01	0.91	1.08	0.87	0.14	0.94	<0.01	<0.01
As -----	28.1	1.92	8.16	4,800	127	<0.01	64.7	813	360	28.8	30.1	9.68	1.42	5.94	9.40
Se -----	42.3	24.0	40.4	<0.01	38.9	<0.01	<0.01	<0.01	<0.01	<0.01	8.81	24.2	<0.01	<0.01	1,150
Te -----	<0.01	<0.01	1.50	<0.01	5.47	6.89	<0.01	<0.01	<0.01	0.58	1.89	0.62	1.34	<0.01	3.40
Hg -----	<0.01	0.51	<0.01	3.61	<0.01	0.31	0.09	0.33	<0.01	0.64	0.50	<0.01	<0.01	3.21	11.0
Tl -----	<0.01	0.29	0.10	212	0.44	<0.01	<0.01	0.46	<0.01	<0.01	<0.01	<0.01	<0.01	1.33	<0.01

Samples:

1. JS-00-28A, lower Niblack Mine dump; pyrite with minor sphalerite and chalcopyrite.
2. LO-99/290, Lookout Mountain Prospect drill core; pyrite with minor chalcopyrite and sphalerite in fine-grained rhyolite.
3. MC-MS, Moira Copper Mine dump; pyrite and chalcopyrite.
4. BI-2-MS, Barrier Islands occurrence No. 2 (Gehrels and others, 1983); pyrite with trace sphalerite.
- 5, 6. JS-00-62E, upper Khayyam Mine dump; pyrite with sphalerite and chalcopyrite.
7. JS-00-36C, Stumble-On Mine dump; pyrite porphyroblasts in massive granular sphalerite.
8. JS-00-29C, Big Harbor East Mine adit; pyrite with abundant chalcopyrite.
9. RT-FS-MS2, Ruby Tuesday (Fish Show) Mine dump; pyrite with sphalerite, galena, and minor chalcopyrite.
10. JS-00-55C, Copper City Mine dump; pyrite with abundant chalcopyrite, minor magnetite, and trace sphalerite.
11. JS-00-56I, Corbin Mine dump; pyrite with abundant sphalerite.
12. JS-00-53D, Keete Inlet Mine dump; pyrite with abundant chalcopyrite and minor sphalerite.
13. JS-00-39A, Nutkwa Main Mine dump; pyrite with abundant sphalerite, minor chalcopyrite, and trace galena.
- 14, 15. JS-00-36D, Stumble-On Mine dump; pyrrhotite with abundant pyrite and sphalerite and minor chalcopyrite.

Table 6. Average composition and ranges in composition of pyrite in sulfide-rich samples from southern Prince of Wales Island and vicinity, southeastern Alaska.

[Minor- and trace-element analyses in parts per million by laser-ablation inductively coupled plasma mass spectrometry at the USGS laboratory in Denver, Colo. the Standard deviation (s.d.) is 1σ value. Grouping of deposits (see table 1) is based on stratigraphic, structural, and metamorphic parameters. Wales Group deposits comprise two samples each from the Khayyam, Ruby Tuesday (Fish Show), and Stumble-On deposits and one sample each from the Big Harbor East, Big Harbor West, Copper City, Corbin, Keete Inlet, Nutkwa Main, and Nutkwa North deposits]

n-----	Wales Group deposits			Moira Sound unit deposits			Barrier Islands deposits		
	Mean	113 S.d.	Range	Mean	27 S.d.	Range	Mean	30 S.d.	Range
Mn-----	1.53	7.75	0.0–72.0	0.44	0.76	0.0–2.90	445	864	0.0–3,552
Co-----	203	366	0.0–2,057	21.6	31.8	0.0–152	46.0	77.8	0.0–315
Ni-----	34.5	71.2	0.0–468	288	968	0.42–4,593	132	220	0.0–874
Cu-----	5.72	7.68	0.0–47.5	7.77	7.97	0.58–31.1	28.5	44.7	0.0–191
In-----	0.11	0.18	0.0–0.97	0.16	0.33	0.0–1.32	0.11	0.14	0.0–0.44
Zn-----	11.2	29.3	0.0–290	8.99	12.6	0.0–55.1	34.6	76.5	0.0–380
Cd-----	1.07	1.67	0.0–7.58	0.95	1.47	0.0–5.71	1.11	1.73	0.0–6.36
Pb-----	0.18	0.36	0.0–3.20	0.18	0.22	0.0–0.84	1.24	1.81	0.0–8.41
Ag-----	0.77	1.11	0.0–5.93	2.53	5.01	0.0–18.3	2.67	4.81	0.0–19.1
As-----	124	382	0.0–3,050	20.8	44.1	0.0–204	1,979	3,679	0.0–14,412
Sb-----	0.39	0.62	0.0–4.03	0.38	0.50	0.0–2.12	39.2	78.6	0.0–283
Bi-----	0.02	0.05	0.0–0.32	0.06	0.12	0.0–0.54	0.02	0.02	0.0–0.10
Hg-----	0.67	1.08	0.0–8.79	0.34	0.52	0.0–1.85	2.21	3.79	0.0–14.9
Tl-----	0.08	0.14	0.0–0.69	0.09	0.14	0.0–0.65	46.4	94.5	0.0–275
Se-----	48.0	143	0.0–1,134	34.1	50.7	0.0–204	45.8	66.0	0.0–224
Te-----	1.20	2.98	0.0–27.3	0.48	0.65	0.0–2.38	0.68	1.37	0.0–7.23
Mo-----	2.90	21.1	0.0–225	88.8	420	0.0–2,186	12.4	46.3	0.0–251
Sn-----	0.73	0.94	0.0–4.79	0.42	0.62	0.0–2.23	0.96	1.29	0.0–6.30

high (100–500 ppm) only in spots containing >1 weight percent Fe. An opposite trend is apparent for Cu, with maximum Cu contents (>100 ppm) measured in the most Fe poor (<0.2 weight percent) spots. Results for Hg are clustered mainly by deposit, with minimum Hg contents (<10 ppm) measured in Fe-rich (>3 weight percent) spots in sphalerite samples from the Khayyam deposit but maximum Hg contents (>100 ppm) measured in sphalerite samples from the Nutkwa Main and Corbin deposits. Significantly, the lowest Hg/Fe ratios in sphalerite were determined in samples from the Khayyam and Stumble-On deposits, which are the most highly metamorphosed, to upper amphibolite grade.

Chalcopyrite

Inclusions of native bismuth in chalcopyrite are inferred by the very high spectral peaks measured for Bi in some samples from the Moira Copper and Niblack deposits. These peaks lack associated As, Sb, Pb, or Ag peaks and so apparently do not reflect residence in a Bi-rich sulfosalt mineral. Native bismuth is considered the likely host, although micro-beam techniques, such as scanning electron microscopy, would be required to confirm this hypothesis. Chalcopyrite from the Moira Copper deposit also has a very high Sn content but not a low Cu or S content, suggesting the presence of stannite or a similar Sn-rich sulfosalt mineral.

Analyses of inclusion-free spots in chalcopyrite (n=40) show relatively low contents (<100 ppm) of most of the trace

elements analyzed (tables 7, 9). However, samples from the Khayyam deposit, in particular, are metal rich, including maximum contents of 252 ppm Ni, 437 ppm Zn, 2,400 ppm Se, and 153 ppm Cd. High Zn contents also were measured in some chalcopyrite grains from other VMS deposits in the study area, with maximum contents of 625 ppm Zn in a sample from the Corbin deposit, 200 ppm As in a sample from the Dama deposit, 1,830 ppm Se in a sample from the Copper City deposit, and 213 ppm In in a sample from the Moira Copper deposit. The high Zn and Cd contents may reflect submicroscopic sphalerite inclusions, whereas the high Ni, Se, As, and In contents probably reflect substitution by these elements within the chalcopyrite lattice: Ni and In for Cu or Fe, and Se and As for S (see Huston and others, 1995; Axelsson and Rodushkin, 2001).

Galena

Galena is abundant only in the Ruby Tuesday deposit but also occurs in other deposits as small grains or inclusions in sulfides. Visible inclusions are generally absent in galena from VMS deposits of the study area (fig. 1). However, very high spectral peaks for some elements suggest the presence of submicroscopic inclusions in the galena. For example, galena from the Ruby Tuesday (Fish Show) deposit locally has high Sb and Ag contents that together imply residence in a sulfosalt mineral, such as tetrahedrite. One sample from the Dama deposit contained galena grains in sphalerite with high Ag

Table 7. Representative minor- and trace-element analyses of sphalerite, chalcopyrite, and galena in sulfide-rich samples from southern Prince of Wales Island and vicinity, southeastern Alaska.

[Minor- and trace-element analyses in parts per million by laser-ablation inductively coupled plasma mass spectrometry at the USGS laboratory in Denver, Colo. N.r., not reported. Minerals: cp, chalcopyrite; gl, galena; sl, sphalerite. All samples contain minor to major amounts of quartz, and some also contain a minor amount of sericite]

Sample ----- Mineral -----	1 sl	2 sl	3 sl	4 sl	5 sl	6 sl	7 sl	8 sl	9 cp	10 cp	11 cp	12 cp	13 cp	14 gl	15 gl
Fe-----	2,990	4,620	2,280	59,100	32,100	9,830	17,800	1,540	N.r.	N.r.	N.r.	N.r.	N.r.	<0.01	<0.01
Mn-----	10.1	38.4	53.2	113	117	127	66.6	11.6	0.50	<0.01	6.73	<0.01	2.35	<0.01	<0.01
Cu-----	86.8	125	15.7	N.r.	14.9	147	N.r.	368	N.r.	N.r.	N.r.	N.r.	N.r.	15.1	<0.01
Pb-----	6.27	1.68	0.37	<0.01	<0.01	7.56	<0.01	11.6	0.44	<0.01	<0.01	0.67	<0.01	N.r.	N.r.
Zn-----	N.r.	N.r.	N.r.	N.r.	N.r.	N.r.	N.r.	N.r.	81.3	<0.01	119	133	5.96	7.54	<0.01
Sn-----	3.49	14.9	4.10	6.93	2.23	10.8	<0.01	46.5	<0.01	10.3	1.55	2.44	19.8	1.81	2.25
Co-----	7.97	<0.01	12.9	0.64	6.04	<0.01	<0.01	<0.01	<0.01	0.79	4.57	<0.01	2.14	<0.01	<0.01
Ni-----	<0.01	17.6	0.74	<0.01	<0.01	<0.01	<0.01	7.23	<0.017	17.0	1.64	<0.01	12.6	<0.01	<0.01
Mo-----	<0.01	<0.01	0.44	33.9	1.08	28.3	42.9	22.1	80.8	3.45	<0.01	<0.01	5.69	3.81	0.33
In-----	140	143	24.4	12.2	4.85	<0.01	33.8	102	64.6	213	2.56	18.1	50.5	0.14	<0.01
Cd-----	2,480	2,220	1,670	1,090	1,480	898	1,520	1,760	<0.01	10.7	6.08	16.9	<0.01	17.3	9.66
Bi-----	3.73	0.65	0.01	<0.01	<0.01	0.66	<0.01	0.26	<0.01	0.23	0.12	0.18	0.12	5.94	0.02
Ag-----	87.5	<0.01	5.77	<0.01	0.36	<0.01	10.0	2.50	29.1	<0.01	17.2	5.41	16.6	453	126
Sb-----	<0.01	4.23	<0.01	<0.01	<0.01	<0.01	38.2	<0.01	13.7	<0.01	<0.01	3.99	<0.01	164	81.4
As-----	8.52	<0.01	4.62	<0.01	1.32	95.2	54.0	20.5	<0.01	<0.01	<0.01	32.1	14.0	<0.01	5.23
Se-----	<0.01	196	102	1,040	99.1	661	1,043	<0.01	1,370	<0.01	646	<0.01	1,830	247	27.3
Te-----	<0.01	34.8	<0.01	4.22	0.06	5.70	15.5	<0.01	21.3	13.1	3.41	<0.01	3.74	<0.01	3.98
Hg-----	24.9	35.7	29.5	16.8	3.46	14.7	229	241	<0.01	<0.01	5.33	3.75	10.8	1.31	0.37
Tl-----	0.50	<0.01	0.52	0.43	<0.01	<0.01	8.94	0.43	6.28	1.49	2.66	<0.01	<0.01	2.59	1.06

Samples:

- 1, 2. LO-53/624.2, Dana Prospect drill core, Niblack area; sphalerite with pyrite and chalcopyrite.
3. LO-99/290, Lookout Mountain Prospect drill core, Niblack area; sphalerite with pyrite and minor chalcopyrite.
4. JS-00-62E, lower Khayyam Mine dump (tram terminal); sphalerite with pyrite and chalcopyrite.
5. JS-00-36C, Stumble-On Mine dump; sphalerite with porphyroblastic pyrite.
6. RT-FS-MS2, Ruby Tuesday (Fish Show) Mine dump; sphalerite with pyrite, galena, and minor chalcopyrite.
7. JS-00-56I, Corbin Mine dump; sphalerite with abundant pyrite.
8. JS-00-39A, Nutkwa Main Prospect dump; sphalerite with pyrite, minor chalcopyrite, and trace galena.
9. LO-53/624.2, Dama Prospect drill core, Niblack area; chalcopyrite with pyrite and minor sphalerite.
10. MC-MS, Moira Copper Mine dump; chalcopyrite with pyrite and trace sphalerite.
11. JS-00-62E, lower Khayyam Mine dump (tram terminal); chalcopyrite with pyrite and minor sphalerite.
12. JS-00-31D, Big Harbor West Mine outcrop; chalcopyrite with pyrite and trace sphalerite.
13. JS-00-55C, Copper City Mine dump; chalcopyrite with pyrite, minor magnetite, and trace sphalerite.
14. JS-00-39A, Nutkwa Main Prospect dump; galena with pyrite and minor sphalerite and chalcopyrite.
15. RT-FS-MS2, Ruby Tuesday (Fish Show) Mine dump; galena with sphalerite, pyrite, and minor chalcopyrite.

Table 8. Average composition and ranges in composition of sphalerite in sulfide-rich samples from southern Prince of Wales Island and vicinity, southeastern Alaska.

[Minor- and trace-element analyses in parts per million by laser-ablation inductively coupled plasma mass spectrometry at the USGS laboratory in Denver, Colo. Standard deviation (s.d.) is 1 value. Grouping of deposits (see table 1) is based on stratigraphic, structural, and metamorphic parameters. Wales Group deposits comprise one sample each from the Corbin, Khayyam, Nutkwa Main, Nutkwa North, Ruby Tuesday (Fish Show), and Stumble-On deposits; Moira Sound unit deposits comprise two samples from the Lookout Mountain Prospect]

<i>n</i> -----	Wales Group deposits			Moira Sound unit deposits		
	Mean	28 S.d.	Range	Mean	7 S.d.	Range
Fe-----	2.43	2.03	0.03–7.46	0.30	0.12	0.21–0.49
Mn -----	121	102	0.0–470	40.2	22.0	3.68–58.4
Co -----	4.56	6.67	0.0–25.4	9.70	7.95	0.0–22.4
Ni-----	8.44	25.4	0.0–121	6.85	5.37	0.74–17.7
Cu -----	83.5	127	0.0–472	41.0	43.3	7.44–114
In -----	29.2	30.4	0.0–102	54.5	49.0	24.4–133
Cd -----	1,465	336	898–2,354	1,928	344	1,616–2,556
Pb -----	1.21	2.65	0.0–11.6	1.45	1.31	0.37–4.16
Ag -----	12.7	19.9	0.0–74.3	17.7	14.3	4.00–44.2
As -----	25.9	42.9	0.0–156	15.0	18.0	0.0–46.7
Sb -----	3.43	8.28	0.0–38.2	0.65	1.44	0.0–3.87
Bi-----	0.09	0.17	0.0–0.66	0.65	1.43	0.0–3.87
Hg-----	71.5	80.3	0.0–241	29.2	9.96	15.6–44.2
Tl-----	0.87	1.92	0.0–8.94	0.18	0.23	0.0–0.52
Se-----	311	424	0.0–1,233	14.6	38.6	0.0–102
Te -----	3.97	8.12	0.0–32.8	1.49	1.97	0.0–5.13
Mo -----	15.4	30.5	0.0–134	5.68	14.3	0.0–38.1
Sn -----	11.3	14.8	0.0–53.8	5.93	6.42	0.0–19.0

and Bi contents, consistent with the presence of other types of sulfosalts inclusion. One galena grain from the Ruby Tuesday (Fish Show) deposit also had a very high Sn content (estimated at >1 weight percent) without a concomitant decrease in S content, implying the presence of stannite or a similar Sn-rich sulfosalt mineral.

Limited data for inclusion-free spots in galena ($n=7$) show uniformly low contents (<20 ppm, table 7) of most of the trace elements analyzed, except in galena from the Nutkwa Main deposit, which has maximum contents of 164 ppm Sb, 247 ppm Se, and 609 ppm Ag. High contents of these elements were also measured in galena from the Ruby Tuesday (Fish Show) deposit, with maximum contents of 97.3 ppm Sb, 949 ppm Se, and 132 ppm Ag. These trace elements probably are hosted mainly within the galena lattice, although the high Ag content could reflect residence in one or more sulfosalts minerals (see Watling and others, 1995).

Sulfur Isotopes

Sulfur-isotopic analyses were performed to determine the sulfur sources of the VMS deposits of the study area (fig. 1) and to assess mineralizing processes. Sulfur-isotopic values of sulfides in the deposits (fig. 7; table 10) mainly range from

–3 to 17 permil, excluding one very low value of –31.1 permil for semimassive pyrite from the Barrier Islands No. 1 deposit. The highest $\delta^{34}\text{S}_{\text{sulfide}}$ values were measured in samples from the Big Harbor East and West deposits. Two groups of samples form isotopic outliers: one with $\delta^{34}\text{S}$ values near 0 permil for sulfides in magnetite iron-formation from the Niblack deposit, and the other with a $\delta^{34}\text{S}$ value of ~3 permil for semimassive pyrite from the Barrier Islands deposits. Massive pyrrhotite and pyrite in separate samples from the Nichols Bay deposit have $\delta^{34}\text{S}$ values of –2.8 and –0.8 permil, respectively. Minor barite in a Mn-rich exhalite associated with the Big Harbor West deposit has a $\delta^{34}\text{S}$ value of 30.6 permil; a similar $\delta^{34}\text{S}$ value of 30.4 permil was measured on a pre-tectonic barite lens in limestone from the Lime Point deposit.

The $\delta^{34}\text{S}$ values for sulfide minerals in the VMS deposits in the Moira Sound unit (fig. 8) range from –2.8 to 10.4 permil (avg 6.1 ± 4.0 permil; $n=22$), overlapping some of those for sulfide minerals in the VMS deposits in the Wales Group, which range from 5.9 to 17.4 permil (avg 11.5 ± 2.7 permil; $n=67$). In comparison, modern sea-floor hydrothermal systems with a significant sedimentary component in their footwall sequences have $\delta^{34}\text{S}_{\text{sulfide}}$ values averaging –5 to 8 permil, with an overall range of 10 to 15 permil (Shanks, 2001). Sulfur-isotopic values for sulfides in Phanerozoic VMS deposits elsewhere show a comparable spread, with $\delta^{34}\text{S}_{\text{sulfide}}$ values averaging 5 to 10 permil over a similar range (Ohmoto, 1986). Thus, the VMS depos-

Table 9. Average composition and ranges in composition of chalcopyrite in sulfide-rich samples from southern Prince of Wales Island and vicinity, southeastern Alaska.

[Minor- and trace-element analyses in parts per million by laser-ablation inductively coupled plasma mass spectrometry at the USGS laboratory in Denver, Colo. Standard deviation (s.d.) is 1σ value. Grouping of deposits (see table 1) is based on stratigraphic, structural, and metamorphic parameters. Wales Group deposits comprise one sample each from the Big Harbor East, Big Harbor West, Copper City, Corbin, Keete Inlet, Khayyam, Nutkwa Main, and Ruby Tuesday (Fish Show) deposits; Moira Sound unit deposits comprise three samples from the Lookout Mountain Prospect and one sample from the Moira Copper Prospect]

n	Wales Group deposits			Moira Sound unit deposits		
	Mean	30 S.d.	Range	Mean	10 S.d.	Range
Zn	88.3	133	0.0–625	70.1	49.0	0.0–143
Mn	5.82	15.9	0.0–88.1	0.66	1.05	0.0–3.19
Co	1.34	2.13	0.0–9.60	0.56	1.04	0.0–3.34
Ni	12.4	45.8	0.0–252	6.81	6.63	0.0–17.0
In	21.3	21.2	0.0–84.6	42.8	63.3	6.46–213
Cd	9.86	27.8	0.0–153	8.79	9.65	0.0–27.4
Pb	0.65	0.97	0.0–3.67	0.37	0.42	0.0–1.19
Ag	14.9	18.2	0.0–94.5	9.23	12.9	0.0–30.0
As	10.7	19.2	0.0–76.1	46.8	73.3	0.0–200
Sb	2.11	3.09	0.0–10.1	3.30	4.64	0.0–13.7
Bi	0.13	0.21	0.0–0.84	0.46	0.53	0.0–1.45
Hg	2.16	3.30	0.0–11.5	1.28	1.34	0.0–3.36
Tl	0.49	0.72	0.0–2.66	1.44	1.94	0.0–6.28
Se	239	563	0.0–2,400	258	465	0.0–1,374
Te	2.61	4.82	0.0–21.0	8.17	8.57	0.0–21.3
Mo	3.36	4.79	0.0–15.5	13.3	25.1	0.0–80.8
Sn	16.9	17.8	0.0–68.3	4.48	5.44	0.0–16.3

its on Prince of Wales Island and vicinity (fig. 1) display fairly typical $\delta^{34}\text{S}$ values for these types of massive sulfide deposit.

Wherever possible, individual sulfide minerals were separated and analyzed for their $\delta^{34}\text{S}$ value to identify potential mineral-mineral fractionations that might be used for sulfur-isotope geothermometry and for calculating primary or metamorphic temperatures. In table 10, $\delta^{34}\text{S}$ data for sulfide minerals are listed in the expected order of fractionation, from isotopically heaviest to lightest: pyrite>sphalerite~pyrrhotite>chalcopyrite>galena. Analysis of these data indicates that most of the sulfide minerals lack significant fractionation, and so sulfur-isotope geothermometry would not be meaningful. The fractionations may be within analytical error because of high-temperature metamorphism. We conclude that the $\delta^{34}\text{S}$ values for individual sulfide minerals in the VMS deposits partially to completely reequilibrated during metamorphism, but that the distinct ranges obtained for different samples reflect original, premetamorphic whole-rock values.

Sulfur-isotopic values of bulk sulfide in country rocks of the study area (fig. 1; table 11) were measured to determine whether the sulfur sources of the hydrothermal systems that formed the VMS deposits could be delineated. The wide variation in $\delta^{34}\text{S}$ values (–10.2 to 19.7 permil) makes source fingerprinting difficult. These $\delta^{34}\text{S}$ values show some differences that broadly correlate with host lithology (fig. 8) but not with host-rock age. In general, metavolcanic rocks contain sulfides with the highest $\delta^{34}\text{S}$ values (1.1 to 19.7 permil), followed by carbonates (–3.7 to 11.3 permil) and siliciclastic metasedimen-

tary rocks (–10.2 to 3.2 permil). Probably most of the siliciclastic rocks, many of which are graphitic, and some of the metacarbonate rocks were affected during diagenesis by bacterial sulfate reduction (BSR) that produced negative sulfur-isotopic values (for example, Machel, 2001). The large negative $\delta^{34}\text{S}$ value (–31.1 permil) for pyrite from the Barrier Islands No. 1 deposit probably records extensive BSR, which likely produced the framboidal texture in some of this pyrite. In the metavolcanic rocks (fig. 8), however, no evidence exists for BSR or the introduction of isotopically light sulfur. Instead, the relatively high $\delta^{34}\text{S}_{\text{sulfide}}$ values of these rocks, far above the typical range for primary sulfide in unaltered volcanic rocks (–1 to 3 permil; Shanks, 2001), probably reflect minor amounts of hydrothermally introduced seawater sulfate that was reduced to sulfide by thermochemical sulfate reduction (TSR). Most likely, these $\delta^{34}\text{S}$ values represent samples from the low-temperature fringes of sea-floor hydrothermal systems that were only mildly affected by VMS-forming processes.

Additional insight can be gained by comparing the $\delta^{34}\text{S}_{\text{sulfide}}$ values of the hydrothermal deposits with those of contemporaneous seawater sulfate (fig. 9). On the basis of the ages of the host rocks, ~500–600 m.y. for the Wales Group and 430–480 m.y. for the Moira Sound unit, and the temporal seawater sulfate curve established by analyzing marine evaporates (Claypool and others, 1980; Ross and others, 1995), we conclude that the higher $\delta^{34}\text{S}_{\text{sulfide}}$ values obtained for the VMS deposits in the Wales Group reflect higher $\delta^{34}\text{S}_{\text{sulfate}}$ values in contemporaneous seawater sulfate. Studies of modern sea-floor massive sulfide deposits (Shanks and others, 1995; Shanks, 2001), together with experimental (Shanks and others, 1981; Seyfried and Shanks, 2004) and theoretical (Janecky and Shanks, 1988) studies of sulfide formation, provide a general framework for understanding sea-floor hydrothermal mineralization. These studies have shown that sulfides in VMS deposits, which have long been known to contain volcanic and seawater sulfur components, form as follows. Seawater sulfate is mostly screened from the circulating hydrothermal system by precipitation of anhydrite and Mg hydroxysulfate at temperatures above 150°C, and the fraction of seawater sulfate that enters the high-temperature hydrothermal system is quantitatively reduced to sulfide. Simultaneously, the seawater-derived hydrothermal fluids leach and dissolve igneous sulfide from footwall rocks, which is mixed with the reduced seawater sulfate to produce $\delta^{34}\text{S}_{\text{sulfide}}$ values intermediate between those of igneous rocks (–0 permil) and contemporaneous seawater sulfate. Although this process can cause a large variation in $\delta^{34}\text{S}_{\text{sulfide}}$ value, in practice the systems tend to be self-regulating. Sulfate reduction is accomplished by iron-bearing minerals and the H_2 they produce during hydrothermal reactions, and in modern systems that have been studied to date, ~10–40 percent of the sulfide derives from reduced seawater sulfate that is added to the mix without apparent sulfur-isotope fractionation.

The sulfur-isotopic data for VMS deposits of the study area (fig. 1) provide strong evidence for formation at or near the sea floor by processes much like those in modern subma-

rine hydrothermal systems. The Wales Group deposits have somewhat higher $\delta^{34}\text{S}$ values because they formed during a period when seawater sulfate had a $\delta^{34}\text{S}$ value near 30 permil, whereas the Moira Sound unit deposits formed during a period when seawater sulfate had a $\delta^{34}\text{S}$ value of ~ 25 permil. Major sulfur sources of the deposits were igneous sulfide and reduced seawater sulfate. The $\delta^{34}\text{S}$ values of disseminated barite in a Mn-rich exhalite from the Big Harbor West deposit (30.6 permil) and in massive barite from the Lime Point deposit (30.4 permil), both of which are in rocks of the Wales Group, support these conclusions, possibly reflecting the sulfur-isotopic composition of contemporaneous seawater sulfate during Late Proterozoic through Cambrian time.

Discussion

Primary Textural and Geochemical Signatures

Whole-rock and mineral compositions of VMS deposits in deformed and metamorphosed sequences reflect various processes, including primary sea-floor mineralization, hydrothermal zone refining in the subsurface, and recrystallization and new-mineral growth during postore deformation and metamorphism (for example, Lydon, 1988; Hannington and others, 1995). In general, sea-floor mineralization in chimney

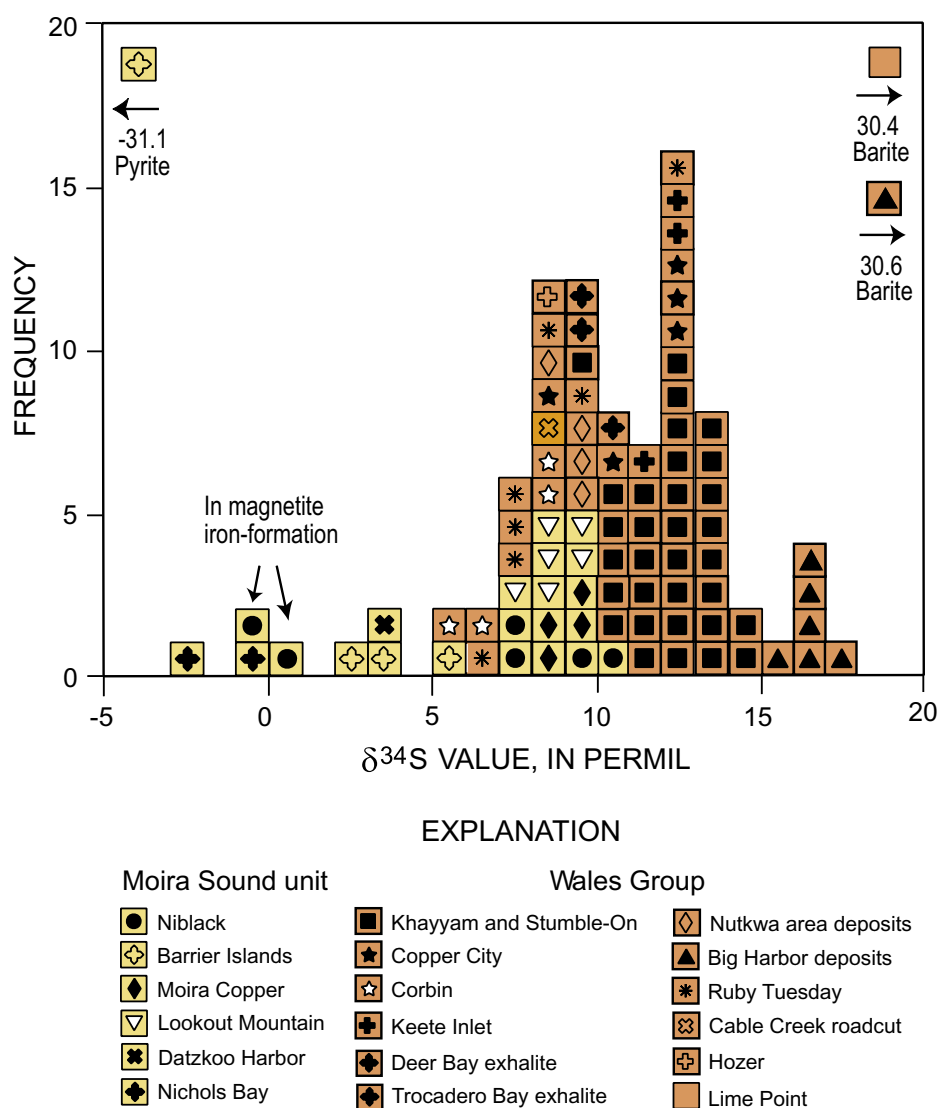


Figure 7. Histogram of sulfur-isotopic values for sulfide mineral separates (pyrite, sphalerite, chalcopyrite, galena, pyrrhotite) from volcanogenic massive sulfide deposits in study area (fig. 1). Isotopically light pyrite sample is from the Barrier Islands No. 1 occurrence; barite sample is from the Lime Point barite deposit. All values in permil relative to Cañon Diablo Troilite standard.

Table 10. Sulfur-isotopic analyses of sulfide minerals and barite in stratabound mineral deposits on southern Prince of Wales Island and vicinity, southeastern Alaska.

[Minerals: cp, chalcopyrite; po, pyrrhotite; py, pyrite; sl, sphalerite]

Sample	Description	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)
Mineral		py	sl	po	cp	Bulk	Barite
Moira Sound unit							
<i>Niblack deposit:</i>							
JS-00-28A	Weakly layered pyritic massive sulfide with minor sphalerite and chalcopyrite.	--	--	--	--	7.0	--
JS-00-28C	Siliceous rock with abundant disseminated fine-grained pyrite and minor chalcopyrite.	--	--	--	--	10.4	--
JS-00-28F	Massive fine-grained magnetite and hematite with abundant seams of pyrite and chalcopyrite.	-0.5	--	--	0.8	--	--
JS-00-28G	Complex mixture of fine-grained magnetite with carbonate, quartz, pyrite, and chalcopyrite.	--	--	--	--	7.9	--
JS-00-28I	Semimassive sulfide (pyrite and subequal chalcopyrite) in chlorite schist with minor quartz and sphalerite.	--	--	--	--	9.9	--
<i>Moira Copper deposits:</i>							
MC-MS-1	Semimassive pyritic sulfide with abundant chalcopyrite and quartz and minor chlorite and sericite.	--	--	--	--	8.8	--
MC-MS-2	Semimassive pyrite with abundant quartz, minor chlorite and sericite, and sparse chalcopyrite.	9.6	--	--	--	--	--
MC-MS-3	Semimassive pyrite with quartz, minor chlorite and sericite, and trace chalcopyrite and sphalerite.	9.0	--	--	--	8.7	--
<i>Lookout Mountain and Dama deposits:</i>							
LO-53/624.2	Layered massive sulfide composed of pyrite, sphalerite, and minor chalcopyrite.	--	--	--	--	9.3	--
LO-61/573.0	Massive sulfide composed of fine-grained chalcopyrite with minor pyrite and matrix quartz and chlorite.	--	--	--	9.5	--	--
LO-99/290	Fine-grained metarhyolite with disseminations and veinlets of chalcopyrite and pyrite, abundant fine-grained sericite, minor sphalerite, and trace galena.	--	--	--	7.5	--	--
LO-99/367	Massive pyritic sulfide with matrix quartz and sericite and trace sphalerite and chalcopyrite.	8.5	--	--	--	--	--
LO-99/378	Altered rhyolite metatuff with abundant disseminated pyrite and minor sphalerite and chalcopyrite.	--	--	--	8.6	--	--

Table 10. Sulfur-isotopic analyses of sulfide minerals and barite in stratabound mineral deposits on southern Prince of Wales Island and vicinity, southeastern Alaska.—Continued

Sample	Description	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)
Mineral		py	sl	po	cp	Bulk	Barite
LO-99/469	Coarse-grained rhyolite lithic metatuff with abundant matrix pyrite, sparse sphalerite, and trace chalcopyrite.	8.7	--	--	--	--	--
<i>Barrier Islands deposits:</i>							
JS-00-58	Sericite-altered rhyolite metatuff(?) with moderate disseminated pyrite and trace sphalerite.	3.4	--	--	--	--	--
BI1-MS	Brecciated fine-grained massive pyrite with quartz and sparse sericite, carbonate, and chlorite.	-31.1	--	--	--	--	--
B12-MS	Semimassive pyrite with abundant sericite, minor quartz, and trace sphalerite and galena.	2.8	--	--	--	--	--
B17-MS	Semimassive pyrite with quartz, chlorite, and minor sericite.	5.1	--	--	--	--	--
<i>Datzkoo Harbor occurrence:</i>							
JS-00-57A	Semimassive pyritic sulfide with trace sphalerite in quartz-chlorite-sericite schist.	3.8	--	--	--	--	--
<i>Nichols Bay Mine:</i>							
B19-MS-1H	Fine-grained massive pyrrhotite (partially oxidized) with abundant diopside(?), minor pyrite, garnet, sericite, and Mn carbonate, and sparse	--	--	-2.8	--	--	--
B19-MS2MS	Fine-grained massive magnetite with minor pyrite and sparse sphalerite associated with abundant Mn carbonate and trace quartz.	-0.8	--	--	--	--	--
Wales Group							
<i>Big Harbor deposits:</i>							
JS-00-29C	Semimassive pyritic sulfide in siliceous schist with abundant chalcopyrite and trace sphalerite.	16.3	--	--	16.6	--	--
JS-00-29E	Quartz-sericite schist with abundant disseminated pyrite and sparse chalcopyrite.	17.4	--	--	--	--	--
JS-00-31B	Chloritic schist with abundant disseminated chalcopyrite and pyrite and sparse sphalerite.	--	--	--	16.4	--	--
JS-00-31D	Semimassive sulfide composed of chalcopyrite, minor pyrite, and sparse sphalerite in chlorite schist.	--	--	--	15.8	--	--
JS-00-32A	Siliceous exhalite composed of quartz, Mn carbonate, minor piemontite and barite, and trace sulfides.	--	--	--	--	--	30.6

Table 10. Sulfur-isotopic analyses of sulfide minerals and barite in stratabound mineral deposits on southern Prince of Wales Island and vicinity, southeastern Alaska.—Continued

Sample	Description	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)
Mineral-----		py	sl	po	cp	Bulk	Barite
84AGKO39E	Quartz vein with margins composed of massive chalcopyrite, minor pyrite, and trace sphalerite with some chloritic wallrock.	--	--	--	16.5	--	--
<i>Ruby Tuesday deposit:</i>							
JS-00-49B	Quartz-rich schist with quartz veins and minor disseminations of pyrite, sphalerite, and galena and trace chalcopyrite.	7.9	8.1	--	--	--	--
RT-81-9/211	Altered rhyolite metatuff(?) with abundant disseminated pyrite (partially laminated), sparse sphalerite and chalcopyrite, and trace galena.	12.3	--	--	--	--	--
RT-FS-MS	Semimassive sphalerite with subequal pyrite and galena and trace chalcopyrite associated with quartz, feldspar, and sparse sericite.	9.5	7.3	--	--	--	--
RT-FS-MS2	Semimassive sphalerite with subequal pyrite and galena, minor chalcopyrite with quartz and sparse sericite, and small volcanic rock fragments.	--	6.2	--	7.1	--	--
<i>Khayyam Mine (main workings):</i>							
JS-00-33B	Sericite-chlorite with disseminations and veins of pyrite, minor chalcopyrite, and sparse sphalerite and magnetite.	10.9	--	--	--	--	--
JS-00-33C	Massive granular pyritic sulfide with abundant matrix chalcopyrite and minor sphalerite.	--	--	--	--	12.4	--
JS-00-33D	Sericite-chlorite with quartz boudins, minor chalcopyrite, pyrite, and pyrrhotite, and sparse sphalerite.	--	--	10.7	10.9	--	--
JS-00-33E	Feldspathic(?) rock with disseminated pyrite and pyrrhotite, minor chalcopyrite, and sparse sphalerite.	--	--	--	--	11.0	--
JS-00-33F	Massive fine-grained pyrrhotite with minor coarse-grained pyrite and pyrite layers, and sparse chalcopyrite and sphalerite.	10.5	--	10.4	--	--	--
JS-00-33G	Massive granular pyritic sulfide in a matrix of chalcopyrite, minor sphalerite, and quartz.	--	--	--	--	12.1	--
JS-00-33K	Feldspathic(?) rock with abundant disseminated pyrite and pyrrhotite, and some disseminated magnetite, sparse chalcopyrite, and trace sphalerite.	--	--	--	9.9	--	--

Table 10. Sulfur-isotopic analyses of sulfide minerals and barite in stratabound mineral deposits on southern Prince of Wales Island and vicinity, southeastern Alaska.—Continued

Sample	Description	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)
Mineral		py	sl	po	cp	Bulk	Barite
JS-00-35B	Sericite-quartz with abundant disseminated pyrite and pyrrhotite, and minor chalcopyrite.	--	--	13.6	14.7	--	--
<i>Khayyam Mine (lower tram terminal):</i>							
JS-00-62A	Massive granular pyritic sulfide with abundant matrix chalcopyrite and minor sphalerite	--	--	--	--	13.0	--
JS-00-62C	Massive granular pyritic sulfide with abundant matrix sphalerite and minor chalcopyrite	12.9	11.3	--	12.0	--	--
JS-00-62E	Massive granular pyritic sulfide with abundant matrix sphalerite and chalcopyrite.	12.4	11.5	--	11.8	--	--
JS-00-62F	Massive fine-grained chalcopyrite with minor sphalerite and sparse quartz.	--	12.1	--	11.9	--	--
<i>Stumble-On Mine:</i>							
JS-00-36A	Massive fine-grained pyrrhotite with abundant chalcopyrite and minor sphalerite.	12.2	12.0	12.3	11.8	--	--
JS-00-36B	Massive granular pyritic sulfide with minor chalcopyrite, interlayered with coarse-grained sphalerite and quartz with disseminated chalcopyrite.	12.9	13.3	--	13.7	--	--
JS-00-36C	Massive granular sphalerite with minor matrix pyrite.	14.2	13.7	--	--	--	--
JS-00-36D	Massive fine-grained pyrrhotite with minor coarse-grained pyrite and minor matrix sphalerite and chalcopyrite.	--	13.4	--	13.4	--	--
JS-00-36E	Chlorite with abundant coarse-grained pyrite, minor pyrrhotite and sphalerite, and sparse chalcopyrite and magnetite.	13.8	--	--	--	--	--
<i>Copper City Mine:</i>							
JS-00-54C	Fine-grained jasper with lenses of coarse-grained magnetite and minor quartz, sparse pyrite and chalcopyrite, and trace sphalerite.	10.3	--	--	--	--	--
JS-00-55A	Fine-grained massive chalcopyrite and sphalerite with minor pyrite and quartz.	--	--	--	--	12.8	--
JS-00-55C	Fine-grained pyritic massive sulfide with minor chalcopyrite and sphalerite and minor matrix quartz.	--	--	--	--	12.7	--
JS-00-55D	Magnetite and chlorite interlayered with quartz, chalcopyrite, and sphalerite.	--	--	--	8.4	--	--
JS-00-55E	Fine-grained massive pyritic sulfide with abundant chalcopyrite, minor sphalerite and quartz, and trace galena.	--	--	--	--	12.8	--

Table 10. Sulfur-isotopic analyses of sulfide minerals and barite in stratabound mineral deposits on southern Prince of Wales Island and vicinity, southeastern Alaska.

Sample	Description	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)	$\delta^{34}\text{S}$ value (permil)
JS Mineral		py	sl	po	cp	Bulk	Barite
<i>Corbin Mine:</i>							
JS-00-56C	Pyritic massive sulfide with abundant matrix sericite and quartz, minor chalcopyrite, and trace sphalerite.	--	--	--	--	8.0	--
JS-00-56F	Quartz-sericite with abundant disseminated pyrite and sparse chalcopyrite.	--	--	--	--	8.6	--
JS-00-56I	Layered/laminated massive sulfide with subequal pyrite and sphalerite, minor quartz, sparse chalcopyrite, and trace galena.	6.4	5.9	--	--	--	--
<i>Nutkwa Prospects:</i>							
JS-00-37A	Quartz-sericite-chlorite schist with abundant disseminated pyrite and trace sphalerite and galena.	9.1	--	--	--	--	--
JS-00-37C	Sericite-chlorite-quartz schist with abundant disseminated coarse-grained pyrite, minor sphalerite, and sparse chalcopyrite.	9.7	--	--	--	--	--
JS-00-39A	Semimassive pyritic sulfide with abundant sphalerite, sparse chalcopyrite and galena, and matrix quartz, sericite, and chlorite.	9.6	--	--	--	--	--
JS-00-39C	Semimassive sulfide with subequal fine-grained pyrite and sphalerite; minor chalcopyrite and trace galena.	--	--	--	--	8.6	--
<i>Keete Inlet Mine:</i>							
JS-00-53A	Pyritic massive sulfide with minor chalcopyrite.	--	--	--	--	12.2	--
JS-00-53C	Semimassive pyritic sulfide with matrix quartz and chlorite.	12.6	--	--	--	--	--
JS-00-53D	Pyritic massive sulfide with minor chalcopyrite, sphalerite, magnetite, quartz, and carbonate.	--	--	--	--	11.4	--
<i>Hozer Prospect:</i>							
JS-00-51A	Quartz-sericite schist with minor disseminated pyrite and trace chalcopyrite.	7.6	--	--	--	--	--
<i>Trocadero Bay exhalite:</i>							
JS-00-42A	Semimassive pyritic sulfide with matrix sericite, chlorite, and quartz.	10.6	--	--	--	--	--
JS-00-42C	Quartz-sericite-chlorite schist with abundant disseminated pyrite.	9.4	--	--	--	--	--
<i>Deer Bay exhalite:</i>							
JS-00-66	Quartz-sericite schist with disseminated pyrite and sparse chalcopyrite.	9.5	--	--	--	--	--
<i>Cable Creek roadcut:</i>							
JS-00-65	Semimassive pyritic sulfide in quartz-sericite schist with trace chalcopyrite.	8.7	--	--	--	--	--
<i>Lime Point barite deposit:</i>							
JS-00-50B	Massive barite (replacement of limestone).	--	--	--	--	--	30.4

Table 11. Sulfur-isotopic analyses of metavolcanic and metasedimentary rocks of southern Prince of Wales Island and vicinity, southeastern Alaska.

Field No.	Description	$\delta^{34}\text{S}$ value (permil)	Latitude (°N)	Longitude (°W)
Moira Sound unit				
00SK220A	Mafic metavolcanic agglomerate.	19.7	54.95694	132.16800
LO-99/512	Unaltered(?) fine-grained greenstone from the Lookout Mountain Prospect, Niblack Mine area; probably stratigraphic hanging wall.	7.5	55.05972	132.14167
LO-99/345	Altered quartz-feldspar porphyry from the Lookout Mountain Prospect, Niblack Mine area; probably stratigraphic footwall.	9.2	55.05972	132.14167
LO-53/630	Altered quartz-eye felsic metatuff from the Dama Prospect, Niblack Mine area; uncertain whether stratigraphic hanging wall or footwall.	11.6	55.05972	132.14167
00SK217A	Felsic metavolcanic breccia.	1.1	54.99745	132.11100
00SK225A	Metalimestone in carbonaceous phyllite.	9.7	54.98308	132.30200
00SK116A	Metalimestone in carbonaceous phyllite.	3.7	55.33098	132.79700
00SK048A	Calcareous wacke turbidite.	-1.4	54.96136	132.94700
00SK009D	Graphitic semischist.	-9.6	54.73742	132.72900
00SK148C	Carbonaceous phyllite.	3.2	54.74082	132.75600
00SK152A	Graphitic phyllite.	3.2	55.24591	132.69300
Wales Group				
JS-00-35C	Garnet-bearing amphibolite from Khayyam deposit; uncertain stratigraphic relations.	13.2	55.29861	132.38611
00SK011A	Amphibolite (metaintrusive).	4.3	54.75697	132.72800
JS-00-34A	Hornblende-bearing felsic gneiss from the Khayyam deposit; uncertain stratigraphic relations.	9.8	55.29861	132.38611
JS-00-29A	Altered massive metarhyolite from wallrock (mine adit) directly adjacent to the Big Harbor East deposit; uncertain stratigraphic relations.	15.1	55.37611	132.95361
JS-00-30	Sulfidic rhyolite crystal metatuff from outcrop ~75 m from adit to the Big Harbor East deposit; uncertain stratigraphic relations.	16.8	55.37611	132.95361
00SK168A	Sericitic marble.	-3.7	55.14529	132.07700
00SK251A	Pyritic black argillite.	-10.2	55.06988	132.10600
00SK327A	Graphitic quartzite.	-7.3	55.34372	132.48342
00SK281A	Graphitic semischist intercalated with felsic metavolcanic semischist.	-6.7	55.21383	132.26500
00SK321A	Pyritic semischist-metavolcanic rock.	-8.0	55.37311	132.37300

structures and exhalites produces fine-grained sulfide and gangue minerals because of relatively fast precipitation during rapid cooling of the hydrothermal fluids. After initial formation on the sea floor, however, chimneys and related sulfide mounds commonly undergo extensive zone refining in which circulating hydrothermal fluids dissolve some minerals, such as anhydrite, recrystallize others, including common sulfides, and precipitate new phases, such as pyrite and amorphous silica. Studies of both modern and ancient VMS deposits that have undergone minimal deformation and metamorphism indicate that hydrothermal zone refining can, in many places, form complex textures and coarse grains in sulfide minerals, including euhedral crystals of sphalerite and pyrite as much as several centimeters in diameter (for example, Eldridge and others,

1983; Petersen and others, 2000; Slack and others, 2003). Primary textures are therefore difficult to identify with confidence in VMS deposits of the study area (fig. 1), except possibly in the Dama deposit, where conspicuous mineralogic layering of sulfides (fig. 2G) likely reflects alternating deposition of pyrite and sphalerite on the sea floor and not later metamorphic segregation, because this VMS deposit in the Moira Sound unit underwent only lower-greenschist-facies metamorphism. Similar layering locally in the Corbin deposit (fig. 3B) is also believed to be primary, although a metamorphic origin cannot be ruled out, given the greater deformational and amphibolite-facies overprint on this older Wales Group deposit.

Primary whole-rock and mineral compositions are believed to generally be preserved in the sulfide-rich samples.

Except in deposits that underwent pervasive metamorphic recrystallization and (or) a high fluid flux during metamorphism, or late faulting, bulk compositions should approximate those that existed during sea-floor and sub-sea-floor mineralization. The major-element contents in sulfide minerals are also interpreted as being mainly primary, except for such VMS deposits as the Khayyam and Stumble-On that were metamorphosed to amphibolite grade. In such sulfides as pyrite from

the Barrier Islands No. 2 deposit (figs. 2H, 3H), very high Mn, As, Sb, Se, and Tl contents (tables 5, 6) likely reflect primary deposition at temperatures below ~250°C (see Huston and others, 1995; Houghton and others, 2004). The very low $\delta^{34}\text{S}$ value (-31.1 permil) of pyrite from this deposit supports this interpretation because such values are generally limited to low-temperature BSR (for example, Machel, 2001). Fe contents in sphalerite are also believed to record early sea-floor

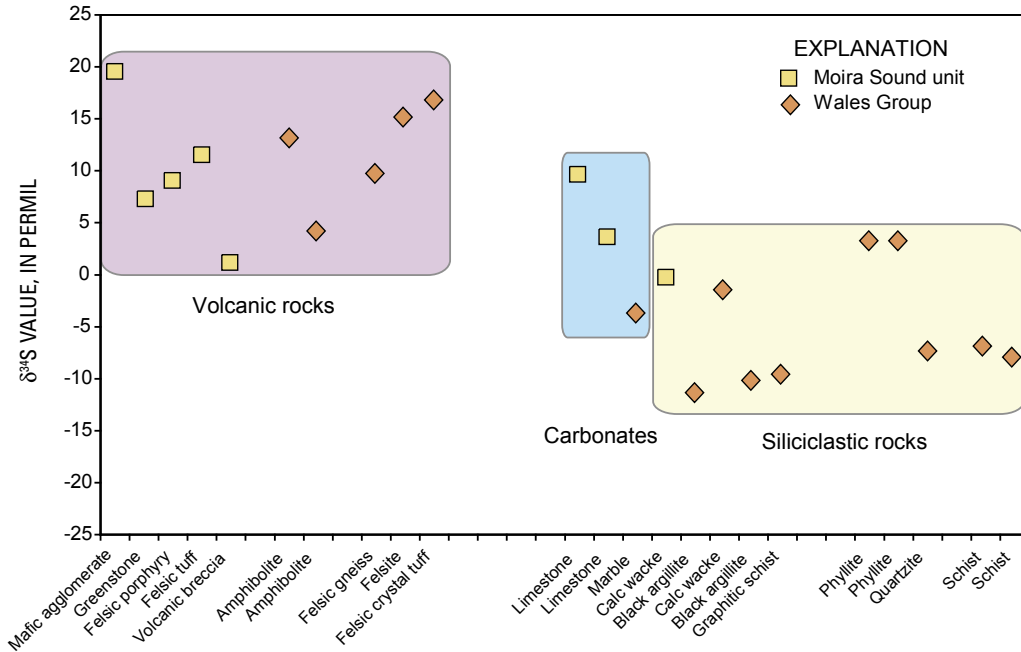


Figure 8. Range of $\delta^{34}\text{S}$ values for disseminated sulfide minerals separated from different rock types of the Wales Group and the Moira Sound unit.

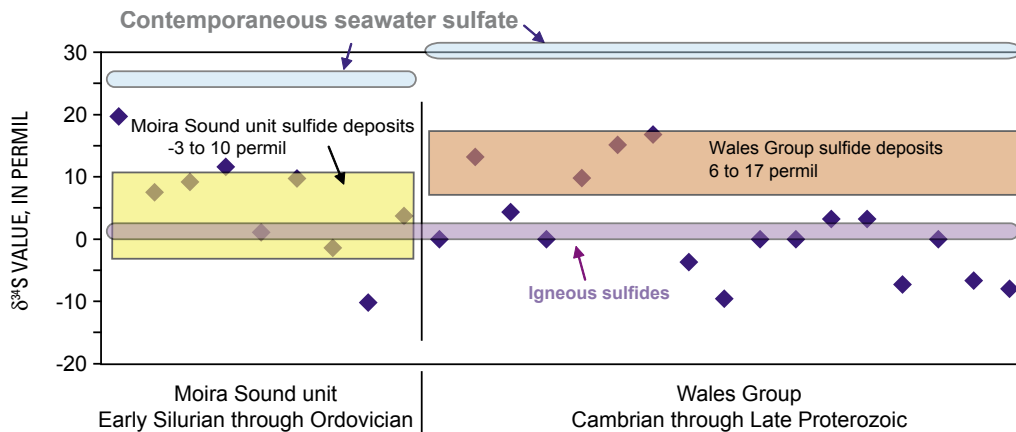


Figure 9. Summary of $\delta^{34}\text{S}$ values for sulfide minerals in volcanogenic massive sulfide (VMS) deposits of the Moira Sound unit (yellow) and the Wales Group (orange). $\delta^{34}\text{S}$ values for igneous sulfides (violet), $\delta^{34}\text{S}$ values for metasedimentary and metavolcanic country rocks (undivided) of the Moira Sound unit and the Wales Group (diamonds) (see fig. 8), and ranges of $\delta^{34}\text{S}$ values for contemporaneous seawater sulfate (blue) during the Ordovician through Early Silurian (Claypool and others, 1980) and the Late Proterozoic (Strauss, 1993; Ross and others, 1995; Hurtgen and others, 2002) are shown for reference. Note that $\delta^{34}\text{S}$ values for sulfide minerals from VMS deposits in the Moira Sound unit and for contemporaneous seawater sulfate are ~5 to 7 permil lower than those for sulfide minerals from VMS deposits in the Wales Group and for contemporaneous seawater sulfate.

and (or) sub-sea-floor hydrothermal processes in deposits that have undergone limited metamorphic overprinting, such as the deposits in the Niblack area in the Moira Sound unit and in the Nutkwa area in the Wales Group. The Fe content in sphalerite from these two deposits varies widely within single thin sections, by as much as 72 and 129 relative percent, respectively. In contrast, the Fe content in sphalerite from the high-grade-metamorphosed Khayyam and Stumble-On deposits varies by no more than 20 relative percent within single thin sections.

Additional support for the preservation of primary geochemical signatures comes from an apparent inverse correlation between Fe contents in sphalerite and average Au contents in the VMS deposits. Except for the Copper City deposit, for which reliable LA-ICP-MS analyses of sphalerite could not be obtained, owing to abundant inclusions of chalcopyrite and other sulfides, the two most Au rich deposits, at Lookout Mountain and Nutkwa (table 2), contain sphalerites with the lowest Fe contents (0.21–0.63 and <0.16 weight percent Fe, respectively) measured in this study. The geologic resource for the Lookout Mountain deposit includes an average of 2.8 ppm Au (Niblack Mining Corp., 2006, URL <http://www.niblackmining.com/>); the average Au content in the Nutkwa Main and North deposits is estimated at 2.3 ppm (table 2). A database of VMS deposits throughout Alaska shows a similar trend, including for the Au-rich Greens Creek ore body on Admiralty Island (avg 5.8 ppm Au; Taylor and others, 1999), in which the highest gold grades (≥ 3 ppm Au) occur in deposits that contain Fe-poor sphalerite (<2 mol percent FeS [<1 weight percent Fe]; Newberry and others, 1997b, fig. 25A). Because such Fe-poor sphalerite is generally pale in color (for example, yellow, light brown), it can generally be easily distinguished in hand specimen from dark-red-brown to black, Fe-rich sphalerite. Preferential occurrence of Fe-poor sphalerite in the gold-rich VMS deposits on Prince of Wales Island and elsewhere in Alaska is consistent with the data of Hannington and Scott (1989), who proposed that such features reflect mineralization at low temperatures (150–250°C) under high-sulfidation (a_{S_2}) conditions. Other aspects of this topic, including applications to mineral exploration, were discussed by Hannington and others (1999).

Effects of Metamorphic Recrystallization

Metamorphic processes have significantly affected most VMS deposits in the study area (fig. 1). The Wales Group deposits were overprinted by three tectonothermal events in the Late Proterozoic, Ordovician, and Early Devonian that in many samples produced new textures, mineral assemblages, mineral compositions, and sulfur-isotope distributions. VMS deposits in the Moira Sound unit were overprinted only by the Early Devonian metamorphic event and so show less deformation, recrystallization, and mineral-specific changes in chemical and sulfur-isotopic compositions. The wide variation in sulfide grain sizes in the Wales Group deposits (figs. 2, 3) reflects

varying degrees of postore deformation and metamorphism, and the extent of fluid flow (flux) associated with these processes, together with the inferred effects of earlier zone refining on and beneath the sea floor. The greatest textural changes occurred at the Khayyam and Stumble-On deposits, where amphibolite-facies metamorphism produced very coarse grained, porphyroblastic pyrite (fig. 2A) and coarse-grained, granoblastic pyrite and sphalerite (figs. 2B, 2C). This metamorphism also formed abundant pyrrhotite (fig. 3A), which is absent from other VMS deposits in the study area except for the Nichols Bay No. 9 and 10 deposits (table 1), which are within the contact aureole of a large granitic pluton. Pyrrhotite commonly forms during high-grade metamorphism of such deposits by the breakdown of pyrite during desulfurization processes (for example, Vokes, 1969; Brooker and others, 1987). Uncommon sulfide-rich veins that cut massive sulfide and metamorphic fabrics in wallrocks at these and other Wales Group deposits probably reflect local remobilization of sulfide minerals by high fluid flow during the Ordovician metamorphic event (see Marshall and Gilligan, 1993; Marshall and others, 2000). Distinguishing effects of the greenschist- to amphibolite-facies Late Proterozoic and Ordovician metamorphic events from those of the greenschist-facies Early Devonian metamorphic event is beyond the scope of this study. However, because the earlier events were characterized by higher temperatures and pressures (Zumsteg and others, 2004), the Early Devonian metamorphism likely produced only minor recrystallization of sulfides and small-scale deformational features, except in areas within or adjacent to Devonian and younger faults or shear zones, which may have focused remobilization of the sulfides, including increased grain sizes (for example, Marignac and others, 2003). The absence of zoned sphalerite in all of the VMS deposits, assuming its original presence based on studies of essentially unmetamorphosed deposits elsewhere (Barton, 1970; Eldridge and others, 1983; Zaw and others, 1996; Slack and others, 2003), probably reflects chemical annealing during all three metamorphic events.

Metamorphic effects on whole-rock and mineral compositions of the sulfide-rich samples are believed to be generally minor. Except in the highly deformed and metamorphosed Khayyam and Stumble-On deposits, the scale of chemical equilibration reached in most of the VMS deposits during the various metamorphic events (combined effects) is estimated at <10 cm. This interpretation is based on widespread trace-element heterogeneity in the sulfide minerals (especially pyrite and sphalerite), as determined by in situ LA-ICP-MS analyses. In theory, if fractionation of trace elements among different sulfide minerals reached equilibrium conditions during metamorphism, these minerals would be mostly homogeneous (for example, Scott, 1983; Huston and others, 1995). However, because evidence for this equilibrium is generally not observed, metamorphic effects on the sulfide compositions were apparently limited spatially. Significant variations in Mn, As, Sb, and Tl contents in pyrite from the Barrier Islands deposits (fig. 6) probably reflects the fact that these are the least deformed and least metamorphosed VMS deposits in the study area.

In contrast to the compositional heterogeneity of sulfide minerals from most of the VMS deposits, those at Khayyam and Stumble-On display a more nearly homogeneous trace-element distribution. This contrast is shown, for example, by the relatively uniform As, Sb, and Tl contents in pyrite and Co, As, Hg, and In contents in sphalerite within the same samples, and even within different samples from the same deposit. Such homogeneity suggests a redistribution of trace elements among the sulfide minerals due to different fractionation factors and higher pressure-temperature conditions than those that occurred during sea-floor and sub-sea-floor mineralization. Some trace elements, such as Hg, were probably lost to the metamorphic fluids, at least partly, during amphibolite-grade metamorphism of the Khayyam and Stumble-On deposits. This process is recorded by whole-rock data indicating that the Hg contents in sulfide-rich samples are about a tenth those in samples from other VMS deposits in the study area, measured at similar Zn contents (fig. 5E). Inclusion-free sphalerite grains from the Khayyam and Stumble-On deposits also have the lowest Hg/Fe ratios, on the basis of LA-ICP-MS data (fig. 6E) that support this interpretation.

Discriminating VMS Deposits in the Wales Group and the Moira Sound Unit

Both geochemical and sulfur-isotopic data may be used to distinguish the VMS deposits in Late Proterozoic through Cambrian rocks of the Wales Group from those in Ordovician through Early Silurian rocks of the Moira Sound unit. A first-order discrimination may be made by using basic geologic information, together with immobile-element geochemical signatures of the metabasaltic host rocks. The stratigraphic settings of a few deposits, however, such as the Copper City and Ruby Tuesday (CC and RTF, respectively, fig. 1), are poorly constrained, and so other criteria are needed for accurate formational assignment. Within the VMS deposits, textures and mineral assemblages are not reliable guides except in such deposits as the Khayyam and Stumble-On (KY and SO, respectively, fig. 1), where high-grade Ordovician metamorphism produced coarse-grained porphyroblastic pyrite, granoblastic pyrite and sphalerite, and abundant pyrrhotite (figs. 2A–2C, 3A). These features are absent in the VMS deposits in the Moira Sound unit, owing to uniformly lower grade overprints during the Early Devonian metamorphic event (Zumsteg and others, 2004). However, because many other VMS deposits in the Wales Group have sulfide textures and sulfide assemblages similar to those in the Moira Sound unit, other criteria must be used to distinguish them. Geochemical data for sulfide-rich rocks

can also provide valuable insight, such as the tendency for the VMS deposits in the Moira Sound unit to have proportionately higher Ag contents relative to base metals and Au, in comparison with those in the Wales Group (fig. 4B).

Sulfur-isotopic data for sulfide minerals in VMS deposits of the study area (fig. 1) can also be used to discriminate the VMS deposits in the Wales Group from those in the Moira Sound unit. Although minor overlap exists, $\delta^{34}\text{S}$ values for sulfides in the Wales Group average ~ 5 to 7 permil higher than for those in the Moira Sound unit (fig. 8). This difference in $\delta^{34}\text{S}_{\text{sulfide}}$ values reflects seawater sulfate as the dominant sulfur source of the VMS deposits, and the related fact that the $\delta^{34}\text{S}$ values of contemporaneous seawater sulfate during the Late Proterozoic through Cambrian were slightly higher than during the Ordovician through Early Silurian.

From a mineral-resource standpoint, base-metal grades vary widely among VMS deposits in both the Wales Group and Moira Sound unit. Overall, the VMS deposits in the Wales Group appear to have a lower potential for high silver grades than those in the Moira Sound unit, whereas the VMS deposits in both groups may have either high or low gold grades. On the basis of limited data, we suggest that future exploration in the study area (fig. 1) for precious-metal-rich VMS deposits should focus on the Moira Sound unit, including the use of Fe-poor sphalerite as a guide to Au-rich VMS deposits. On Prince of Wales Island, such Fe-poor sphalerite is characteristically yellow or yellowish brown and is generally discernible in both hand specimens and drill cores. The Copper City and Nutkwa areas, which are underlain by the Wales Group, also have a potential for Au-rich VMS deposits (table 2).

Acknowledgments

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